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SYNTHETIC POLYAMIDE TEXTILE MATERIAL HAVING A POLYORGANOSILOXANE GRAFTED THERETO

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5 Claims. (Cl. 8—115.5)

This application is a continuation-in-part of application Serial No. 500,033, filed April 7, 1955, which is now abandoned.

This invention relates to a process and product. More particularly it concerns a process for graft copolymerizing a polyorganosiloxane to a textile produced from a polyamide and the product formed thereby.

It is an object of the present invention to provide a process for graft copolymerizing a polyorganosiloxane to a textile produced from a polyamide.

Another object is to provide a novel and useful textile formed from a polyamide substrate to which a polyorganosiloxane is graft copolymerized, thereby rendering the said textile water repellent.

These and other objects will become apparent in the course of the following specification and claims.

In accordance with the present invention, a textile produced from a polyamide of fiber-forming molecular weight in intimate contact with a polyorganosiloxane, is subjected to ionizing radiation to produce graft copolymerization between the textile and the polyorganosiloxane.

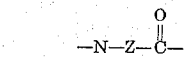
By "ionizing radiation" is meant radiation with sufficient energy to remove an electron from a gas atom, forming an ion pair; this requires an energy of about 32 electron volts (ev.) for each ion pair formed. This radiation has sufficient energy to non-selectively break chemical bonds; thus in round numbers radiation with energy of 50 ev. and above is effective for the process of this invention. The ionizing radiation preferred for forming free radicals and initiating grafting on the synthetic linear condensation polymer of this invention is high energy ionizing radiation, and has an energy equivalent to at least 0.1 million electron volts (mev.). Higher energies (10 to 15 mev.) are even more effective; the only known upper limit is imposed by available equipment. This radiation is generally classed in two types: high energy particle radiation, and high energy ionizing electromagnetic radiation. The effect produced by these two types of radiation is similar, the essential requisite being that the incident particles or photons have sufficent energy to break chemical bonds and generate free radicals.

By "high energy particle radiation" is meant an emission of high energy electrons or nuclear particles such as protons, neutrons, alpha particles, deuterons, or the like, directed so that the said particle impinges upon the solid polymer bearing the unsaturated amide. The charged particles may be accelerated to high speeds by means of a suitable voltage gradient, using such devices as a resonant cavity accelerator, a Van de Graaff generator, a betatron, a synchrotron, cyclotron, or the like, as is well-known to those skilled in the art. Neutron radiation may be produced by bombardment of selected light metal (e.g. beryllium) targets with high energy positive particles. In addition, particles radiation suitable for carrying out the process of the invention may be obtained from an atomic pile or from radioactive isotopes or from other natural or artificial radioactive material.

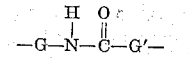
By high energy "ionizing electromagnetic radiation" is meant radiation produced when a metal target (e.g., gold or tungsten) is bombarded by electrons possessing appropriate energy. Such energy is imparted to electrons by accelerating potentials in excess of 0.1 million electron volts (mev.), with 0.5 mev. and over preferred. In addition to X-rays produced as indicated above, ionizing electromagnetic radiation suitable for carrying out the process of the invention may be obtained from a nuclear reactor ("pile") or from natural or artificial radioactive material, for example, cobalt 60. In all of these latter cases, the radiation is conventionally termed gamma rays.

The irradiation is carried out using a Van de Graaff electron accelerator with an accelerating potential of 2 million electron volts (mev.) with a tube current of 250 to 290 microamperes. Samples to be irradiated are placed on a conveyor and traversed back and forth under the electron beam at a distance of tube window to sample of 10 cm. The conveyor speed is 40 inches per minute. At the sample location the irradiation intensity is 12.5 watt sec./cm.^{2} of sample which is approximately equivalent to an available dose per pass of one mrad.

By the term "textile produced from a polyamide" is meant a fabric, fiber, filament, yarn, pellicle, flock and the like produced from a linear polyamide containing recurring units of the formula:



wherein Z is a member of the class consisting of a divalent hydrocarbon radical and a divalent radical of the formula



wherein G and G′ are divalent hydrocarbon radicals. Typical polyamides and processes for their production are described in United States Patents Nos. 2,071,250, 2,071,253 and 2,130,948. Among the specific polyamides included within the present invention are those formed by the condensation polymerization of a dibasic acid or an amide-forming derivative thereof, such as adipic, sebacic, suberic, azelaic acids or the like, and a diamine such as piperazine, bis-amino cyclohexane, ethylene, tetramethylene, pentamethylene, hexamethylene, decamethylene, paraxylylene diamines and the like. Such materials may also be formed by other well known methods such as by polymerization of amino acids or caprolactam.

The following example is cited to illustrate the invention. It is not intended to limit it in any manner. The "standard washing" to which samples are subjected consists of a 30-minute immersion in 70° C. water containing 0.5% of detergent (sold under the trademark "Tide" by Procter & Gamble Co. of Cincinnati, Ohio), in an agitation washer. Radiation dosages are given in units of "mrep" (millions of roentgen equivalents physical), a "rep" being the amount of high energy particle radiation which results in an energy absorption of 83.3 ergs per gram of water or equivalent absorbing material.

Example

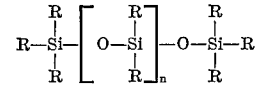
A sample of fabric woven into a taffeta weave from 70 denier polyhexamethylene adipamide continuous filament having a denier per filament of 0.2 is immersed in a liquid polydimethyl siloxane (DC Fluid 550, manufactured by Dow-Corning Corporation of Midland, Mich.). After squeezing out the excess liquid, but while still wet, it is enclosed in an aluminum foil wraper and subjected to electron irradiation in a 1 mev. resonant transformed with a beam-out current of 560 microamperes. The sample is placed on a conveyor belt which carries it through the electron beam at a rate of 16 inches per minute. At the sample location, the beam supplies irradiation of 6.7×10^6 reps (6.7 mrep) per pass. The sample

is traversed back and forth across the beam until a total dose of 40 mrep is attained, thereby graft copolymerizing the polyorganosiloxane to the polyamide. After 15 consecutive standard washings, the sample is dried and tested for ease of wetting by placing a 0.3 inch diameter drop of water on the dry fabric and measuring the diameter of the wet spot after 60 seconds. The water drop on the siloxane coated, irradiated sample spreads to a diameter of 0.5 inch. A drop on an uncoated, irradiated comparative control spreads to 1.5 inch. Repetition of the process substituting "X-rays" for particle irradiation to an equivalent dosage produces a similarly water-repellent graft copolymerized product. A sample of the fabric treated with the silicone oil (but not irradiated) and thereafter subjected to 15 consecutive standard washings has no greater water repellency than the original, uncoated fabric. About 0.001% by weight, based on the graft-copolymerized textile, of graft copolymerized polyorganosiloxane is adequate to produce some water repellency. Grafting to produce at least about 0.01% grafter polyorganosiloxane is preferred. Higher weight gains of 1%, 5% or even 15% may sometimes be desirable, especially for polymer blends.

The textile to which the polyorganosiloxane is graft copolymerized acts as a substrate, the graft copolymerization being evidenced by failure of solvents to thereafter separate the polyamide and polyorganosiloxane constituents. The shape of the polyamide textile to which the polyorganosiloxane is adhered is not critical. Thus the process of the present invention may be applied to a funicular structure such as a continuous filament, a spun yarn, staple, or the like. It may likewise be applied to a pellicle or a fabric of ordered or randon intertwined reticulation such as woven, knitted, plaited, twisted, felted, fused or other construction. Furthermore, the shaped article may be in the form of finely comminuted particles which may, after having the polyorganosiloxane adhered to it, be melted and shaped by extrusion, molding or casting, into a different form.

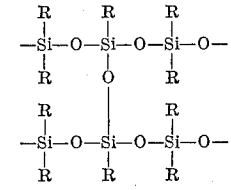
In the practice of the present invention, it is not necessary that the polyorganosiloxane be coated upon the polyamide textile. The polyamide resin and the polyorganosiloxane can be mixed by milling or the like and then exposed to ionizing irradiation after forming of the textile structure or (if a drawable fiber or film) after drawing, whereby adherence is induced. Similarly the polyorganosiloxane may equally well be added to the polyamide in the melt or in solution, the substrate shaped by extrusion, molding or casting and the graft copolymerization may then be developed by ionizing irradiation of the shaped article as previously described. It is obvious that any of the above methods of application will produce a polymeric textile material with the modifier dispersed throughout and adhered to the organic polymeric matrix.

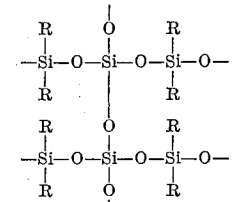
The polyorganosiloxanes which are employed in the present invention are commonly referred to as "silicone fluids." These materials are well known and are more fully described in the book "An Introduction to the Chemistry of the Silicones" by E. G. Rochow (John Wiley & Sons, Inc., New York, 2nd ed., 1951). Among the useful representations of the silicones is the following:



wherein the R's represent the same or different hydrocarbon radical such as the members of the class consisting of the alkyl, aryl, alkylaryl, and aralkyl radicals and n is a number greater than 1 and having a degree of polymeriztion such that the polyorganosiloxane is fluid at a temperature below about 150° C. Mixtures of varying chain length are suitable. The orientation and nature of the various hydrocarbon substituents in the

molecular structure has not been found to be of importance, however it is preferred that the siloxane chain is of at least sufficient length to be a liquid. Those polyorganosiloxanes having branched, cross-linked structures, indicated by partial formulas:





or

are also suitable.

The R's in the formula may be all the same or may be different depending upon the method of preparation. Furthermore, these R's may contain reactive groups or may be readily susceptible to oxidation, such that heating the silicone causes it to react further to form a more completely cross-linked structure which is insoluble and infusible, i.e. the silicone is thermoset.

It has been observed that irradiation of the coated textiles in the presence of air or moisture may increase the susceptibility of the product to degrade. This can be avoided by employing an atmosphere of inert gas around the article while it is being irradiated. Alternatively, a satisfactory and simpler approach is to wrap the sample in a material which is substantially air and water impervious, thus limiting the quantity of air or moisture contacting the sample. The samples may be wrapped in polyethylene film. The nature of such wrapping material is not critical, provided it is substantially impervious to air and moisture. Aluminum foil is satisfactory.

It is within the scope of this invention to include in the combination to be irradiated, materials which may have a protective or antioxidant effect in preventing radiation degradation of either modifier or substrate or both. Compounds of this type are cysteine, carbon and the like. It is also within the scope of the invention to include in the combination to be irradiated materials which absorb radiation and transmit the energy thus absorbed to the modifier or the organic polymeric materials or both, whereby adhering is promoted and the efficiency of utilization of radiation is increased. Compounds with this property are somewhat similar to sensitizers in photography, except that in this case useful materials absorb high energy radiation and emit the energy in a lower or more usable range. Phosphor screens containing calcium tungstate, zinc sulfide or metallic lead or the like have utility for this purpose. The phosphor materials may be used as plates contacting the material being treated, or may be incorporated in the modifying agent or even be coated on or dispersed in the organic polymeric material which it is desired to modify.

The irradiation may be accomplished over a wide range of temperatures. However, a low temperature decreases the tendency toward oxidation. Since the absorption of the radiations frequently causes a temperature increase in the range of about 2° C. for each mrep absorbed, if high tube current is employed so that absorption is complete within a short time interval, it is usually advisable to provide means to remove the heat generated to avoid injury to the sample. The use of Dry Ice to maintain a

cold atmosphere is very satisfactory for this purpose. In general, irradiation at a higher temperature promotes the speed with which bonding occurs, thus promoting a higher throughput of a given piece of equipment at a constant radiation dosage. Temperatures as low as —80° C. and as high as 150° C. may be employed. Maintenance of the temperature of the sample within the range of from about 0 to about 75° C. is preferred.

In determining the optimum dose of irradiation for any particular combination, both the nature of the polyorganosiloxane and the nature of the polyamide textile must be considered. For those polyorganosiloxanes having one or more substituent R groups containing units of aliphatic unsaturation, irradiation dose of 0.05 mrep is usually sufficient to initiate the grafting reaction. Better results are usually obtained at a dose of 0.1 mrep. For non-polymerizable, saturated polyorganosiloxanes a minimum dose of one mrep is recommended. In general, a dose of about 5 mrep is adequate to initiate the bonding. It is preferred to use at least a dosage of about 15 mrep. Higher dosages may be used and are frequently highly beneficial. Dosages so high that substantial degradation of the shaped substrate occurs must obviously be avoided. As a guide in this regard, fibers produced from polyhexamethylene adipamide may be irradiated to a dosage as high as 80 mrep. However, it is preferred that the dosage applied to these substrates not exceed about 60 mrep. At constant temperature the degree to which the substrate is affected by the polyorganosiloxane graft copolymerized to it will depend upon the nature of the substrate, the nature of the polyorganosiloxane graft copolymerized and the amount of irradiation to which the textile bearing the polyorganosiloxane is subjected. The concentration of the polyorganosiloxane upon the substrate will also affect the ultimate results. In general the polyorganosiloxanes are applied to the substrate as liquids or solutions, the solutions being of relatively high concentration. Such procedure provides the maximum opportunity for the polyorganosiloxanes to be bombarded by the high energy particle.

Prior to treatment, the shaped article, such as a filament, may be oriented by hot or cold drawing. It may contain fillers such as pigments, antioxidants, polymerization catalysts and the like. After the irradiation the product may be after-treated. Frequently a certain amount of decomposition occurs at the surface which is readily removed by washing in detergent. In other after-treatments, the textile may be dyed, bleached hot or cold drawn, chemically reacted, or given coatings of lubricants, sizes or the like or other similar treatments.

To be efficient in the practice of the present invention, it is necessary that the radiation have sufficient velocities to permit penetration of several layers of material, when fabrics or films are being treated. The velocity required will depend on the nature of the particle and also on the nature of the substrate to a certain extent. An electron particle which is under acceleration by a potential of a million volts (mev.) will penetrate a thickness of polyhexamethylene adipamide of about 0.25 cm. regardless of the form of the shaped article, i.e., the nature of the weave, denier or filament, whether the textile is solid, or a fabric formed from filamentous materials. Acceleration of electrons by 2 mev. will penetrate a shaped article having a thickness of ½ cm. In situations where surface effects are paramount, it is not necessary that the textile be completely penetrated by the high energy particle and lower accelerations may be employed. Under these conditions, if the surface effect is to be applied to both sides of the shaped article, it will obviously be necessary to expose each of the surfaces to the particle radiation. This is done by simultaneously bombarding both sides of the shaped article or alternatively by subjecting each side to the single source of irradiation during different runs.

The polyorganosiloxane may be applied to its shaped substrate by immersion, padding, calendering, spraying, exposure to vapor condensation, or by other similar means. It is sometimes desirable to remove excess liquid by squeezing prior to exposure to irradiation. Alternatively, the polyorganosiloxane may be deposited upon the textile substrate by flashing off the solvent in which it is dissolved prior to application.

The process of the present invention is valuable in creating surface effects upon textiles. It may be employed upon textiles to affect softness, resilience, tendency to shrink, static propensity, dyeability, resistance to hole melting, pilling, hydrophilicity, wickability, and the like. It is useful in varying such properties as tenacity, elongation, modulus, creep, compliance ratio, work recovery, tensile recovery, decay of stress, wet properties, high-temperature properties, abrasion and wear resistance, moisture regain, flex life, hydrolytic stability, heat-setting properties, boil-off shrinkage, dry-cleaning properties, heat stability, light durability, zero strength temperature, melting point, soilability, ease of soil removal, laundering properties, liveliness, crease resistance, torsional properties, hysteresis properties, fiber friction, dyeability (depth, rate, permanence and uniformity), printability, washfastness of dyes or finishing treatments (resins, ultraviolet absorbers, etc.), handle and drape properties (stiffening or softening), pilling, heat-yellowing, snag resistance, elasticity, density, ease in textile processability, solubility (insolubilization or increase in solubility), bleachability, surface reactivity, delustering action, drying properties, fabric life, crimpability, stretchability, fabric stabilization, compressional resilience (rugs), thermal and electrical conductivity, transparency, light transmittance, air and water permeability, fabric comfort, felting, ion exchange properties, adhesion, over-all appearance and combinations of these as well as others.

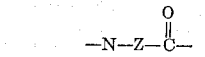
In addition to the above modifications there are other modifications which would be particularly useful in fabrics and synthetic papers. By way of illustration, fabrics may be modified to improve adhesion to various coating or laminating agents which it may be desirable to adhere thereto, to change "slip" or the ease with which one sheet slides over another, to produce non-reflective or decorative coatings on fabrics or sheets, to improve the ease of printing colors on such sheets and many other modifications such as will readily suggest themselves to one skilled in the art.

It is apparent that those properties which are not primarily a function of surface characteristics (e.g., tenacity, elongation, modulus, and the like) may be more conveniently modified by incorporating the modifiers in the polymeric matrix of the textile and then subjecting it to particle irradiation to develop adherence. It is also apparent that at times it may be desirable to incorporate one or more modifiers in the matrix and coat one or more modifiers on the surface of the polymer, then develop adherence simultaneously by irradiating the shaped textile article.

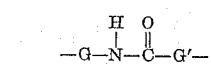
Many other modifications will be apparent to those skilled in the art from a reading of the above description without a departure from the inventive concept.

What is claimed is:

1. A water repellant textile formed from a polyamide selected from a linear polyamide containing recurring units of the formula



wherein Z is a member of the class consisting of a divalent hydrocarbon radical and divalent radical of the formula



wherein G and G' are divalent hydrocarbon radicals, having a polyorganosiloxane graft-polymerized thereto, the said polyorganosiloxane being graft polymerized to

the said linear polyamide by ionizing radiation having an energy from about 50,000 ev. to about 100 mev. at a radiation dose of from about 0.05 mrep to about 80 mrep.

2. The structure of claim 1 wherein the said textile is in the form of a fabric.

3. The structure of claim 1 wherein said textile is in the form of a yarn spun from staple fiber.

4. The structure of claim 1 wherein the said textile is in the form of a continuous filament.

5. The structure of claim 1 wherein the said textile contains at least 0.001% polyorganosiloxane as the co-graft-polymerized constituent of the said polyamide.

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J. CANNON, *Assistant Examiner.*