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# DYEABLE CHLOROMETHYLSTYRENE-VINYL-GRAFTED POLYPROPYLENE FIBERS AND PROCESS OF PRODUCING SAME

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The present invention relates to a light and thermally stable, chemically modified, preformed polypropylene fiber. More particularly, it relates to a light and thermally stable, preformed, vinyl-grafted, uniformly dyeable polypropylene fiber, and to methods for preparing the same. Still more particularly, it is concerned with a thermally stable, light-stable, preformed, chloromethylstyrene-grafted polypropylene fiber compatible with wool, cotton and other fibers and capable of being uniformly dyed, as well as with dyed polypropylene fibers and with methods for preparing the same.

It is known that preformed polypropylene fibers of high average molecular weight in the range of from about 100,000 to about 500,000 are manifestly unsuitable as textile fibers. They possess undesirably low sticking temperatures in the range of about 140° C. and are found to be heat-unstable, waxy to the touch, nondyeable and, in general, relatively inert to all aftertreatments. For instance, when such fibers are subjected to moderate heat as that developed during ironing of a fabric prepared therefrom, the fibers either discolor, partially fuse or melt. In view of the increased demand for uniformly dyeable, light-stable, heat-stable, high sticking temperature-polypropylene fibers, it would be highly desirable to provide such fibers so as to meet a long-felt need.

It is, therefore, a principal object of the present invention to provide a uniformly dyeable, heat-stable, preformed, colorless, vinyl-grafted polypropylene fiber of good tensile strength and possessing a spongy structure. It is a further object to provide a novel method for obtaining a uniformly dyeable, heat-stable, light-stable, preformed fiber of good tensile strength. It is still a further object to provide either a colorless or dyed, preformed, heat-stable, light-stable polypropylene fiber of good tensile strength and a good sticking temperature. Other objects will be apparent to those skilled in the art from a consideration of the detailed description herein.

To this end, a heat-stable, light-stable, colorless, uniformly dyeable, preformed polypropylene fiber of good tensile strength is provided utilizing an overall straightforward method in its preparation. In its broadest aspects, the method involves irradiating a chloromethylstyrene-swollen, preformed polypropylene fiber in the presence of a polymerizable vinyl monomer and a cross-linking agent. Fiber so-modified is rendered readily dyeable. Reaction of the fiber with a nucleophilic reagent can occur swiftly prior to the dyeing operation and dyestuffs can be more evenly distributed throughout the fiber. Surprisingly, no sticking temperature is observed within the range of 25° C. to 270° C.

According to the overall process of the invention, preformed polypropylene fiber is initially irradiated while causing the fiber to be contacted with a chloromethylstyrene monomer in the presence of a polymerizable vinyl monomer and a cross-linking agent which are provided in specific amounts. Dyeing of such treated fiber can be carried out in the presence of dyestuffs in a suitable organic medium. Alternatively, dyeing can occur in an aqueous medium, in the absence of an organic solvent, usually at temperatures ranging from about 15° C. to about 150° C., when the so-treated fiber is subjected to a prior treatment with a nucleophilic reagent, such as an amine, ammonia, an alkali metal sulfite, an alkali metal bisulfite, or an alkali metal sulfide.



The preformed polypropylene fiber to be treated is a linear, isotactic polymer of weight-average molecular weight equal to from about 100,000 to about 1,000,000 and, preferably, from about 250,000 to about 750,000. In general, the preformed, untreated fiber possesses a "waxy" hand and is insoluble in most organic solvents.

In order to render the preformed polypropylene fiber amenable to uniform dyeing and to impart the above-noted properties thereto, it has been found that the fiber can be modified utilizing any one of several techniques. The modification, in essence, involves the grafting to the fiber of a mixture of chloromethylstyrene and a vinyl monomer in the presence of a cross-linking agent. One method involves the simultaneous contact of the latter mixture and the preformed polypropylene fiber in the substantial absence of oxygen while subjecting the fiber so-swollen with the monomers to ionizing irradiation. Another method for achieving modification of the fiber is to irradiate initially the preformed fiber by means of ionizing radiation to form free radicals throughout the fiber and then to immerse the so-irradiated polymer in the aforementioned monomeric mixture. The latter technique is similarly conducted in the absence of oxygen. Still another method is to irradiate the preformed polymeric fiber in the presence of oxygen-containing gas (e.g., air) to form a mixture of hydroperoxides both on the fiber and in the fiber, and then to heat the latter in the presence of the aforementioned mixture and in the absence of oxygen so as to graft the chloromethylstyrene, vinyl monomer and cross-linking agent on to the polymeric molecules throughout the fiber.

Radiation utilized in the process of the invention can be of several types. One type is particulate radiation, such as $\alpha$-particles and $\beta$-radiation (electrons), obtained from radioactive nuclei or high-energy electrons from machine sources. Another type of radiation may be electromagnetic radiation, such as gamma-rays or X-rays. However, the preferred source of radiation is a beam of high-energy electrons possessing energies in the range of from about 0.02 mev. to 20 mev., and preferably in the energy range of from about 0.05 mev. to 4 mev. For optimum operation, a beam of electrons of 0.5 mev. has been found to be eminently satisfactory for the treatment of most thicknesses of carded staple fiber, tow fiber or even woven fabric.

It has been observed that for ionizing radiation a total dose as low as 5,000 rads and as high as 20,000,000 rads can be effectively tolerated. Optimum results, however, are obtained when doses from 7,500 to 1,000,000 rads are employed in the grafting procedure so as to render the fiber substantially free from the "waxy" hand as well as to impart enhanced uniform dyeability with little or no attendant loss of mechanical strength. Surprisingly, the original low sticking temperature of the fiber is no longer found. Rather no measurable sticking temperature up to 270° C. is observed.

In general, the chloromethylstyrene monomer reactant may be either ortho-, meta- or para-chloromethylstyrene or mixtures of the same in various proportions. Although chloromethylstyrene is exemplified herein, it is understood that a wide variety of styrenes, such as bromomethylstyrene, chloromethylstyrene with other substituents such as halogen, alkyl or aryl groups on the ring, as well as $\alpha$-halo- or $\alpha$-alkyl-substituted chloromethylstyrenes may be used in the practice of the invention.

Illustrative vinyl monomers which may be used in conjunction with the chloromethylstyrene or its analogs

are: styrene, methylstyrene, acrylonitrile, methylmethacrylate and equivalents thereof.

Admixed with the aforementioned monomers are cross-linking agents exemplary of which are: divinyl benzene, bismethylene acrylamide, triallyl cyanurate, tetraallyl melamine, hexaallyl melamine and diallyl sebacate.

For optimum results, the chloromethylstyrene and vinyl monomer are supplied in sufficient amounts to swell the fiber and simultaneously provide grafts which fall within the following ranges based on the overall weight of the polymeric fiber. The graft provided by the chloromethylstyrene monomer falls within the range of from about 1% to about 10%, and preferably between 4% and 8.5%. The graft provided by the vinyl monomer other than the chloromethylstyrene monomer ranges from about 10% to about 30%, and preferably from about 13% to 16%. The cross-linking agent is provided in such amounts as to form a graft contributing to an overall weight increase in the polymer ranging from about 1% to about 10%. Observance of the foregoing ranges is essential to obtain a polypropylene fiber having a wool-like hand, no observable sticking temperature to temperatures ranging from 25° C. to 270° C., improved color fastness to washing, improved water-retention, improved antistatic behavior of the fiber as well as dyeability to deep, uniform intense shades.

Extremely short periods are required for delivering ionizing radiation in the form of high-energy electrons. It has been found that an exposure time in the range of from about 0.06 to about 0.6 second is sufficient for delivering the necessary dose of ionizing radiation in the form of electrons. However, longer periods are usually required when using ionizing radiation in the form of electromagnetic waves. Thus, unless unusually large sources should become available, which are able to supply very high dose rates, some ten to fifteen minutes may be required where X-rays or gamma-rays are used. When employing such ionization techniques, a broad range of temperatures, usually between about 20° C. and 150° C., can be employed to accomplish such modification.

In general, the grafting step is carried out heterogeneously in the absence of oxygen. For instance, a solid preformed polypropylene fiber and a mixture of a liquid chloromethylstyrene, a polymerizable vinyl monomer and a cross-linking agent are contacted in such an oxygen-free environment. Swelling of the fiber by the aforementioned monomeric mixture is most readily induced by employing increased temperatures, usually between 40° C. and 120° C. However, the use of pressure employing an inert gas such as nitrogen or any of the rare gases to expedite the penetration of the monomer mixture into the fiber is also contemplated. Alternatively, the grafting procedure may be carried out heterogeneously by contacting the polypropylene fiber with the monomeric mixture in the vapor phase. In so-proceeding, a multiplicity of short grafts spaced and cross-linked at fairly regular intervals along the polypropylene chain appears to occur. So-grafted, preformed, colorless polypropylene fibers possessing high tensile strength and uniformly enhanced dyeability may be dyed in an organic medium, such as dimethylformamide. Alternatively, the fibers may be dyed in a conventional aqueous environment by causing a nucleophilic or electron-donating reagent in the solid, liquid or gaseous state to react with them, and thereafter subjecting resultant fibers to dyeing at temperatures in the range of from about 20° C. to about 150° C., and preferably from about 25° C. to about 100° C.

The nucleophilic reagent can be added to chloromethylstyrenated and styrenated, cross-linked, preformed polypropylene fiber. Alternatively, the so-treated fiber may be added to the nucleophilic reagent, if desired. The order of addition is not critical. Where the nucleophilic reagent is a normally solid material, such as alkali metal sulfides or sulfites, a solvent therefor is employed as a carrier. For instance, dimethylformamide can be used for such purpose. Where the nucleophilic reagent is a liquid, such as certain tertiary amines, diamines, hydroxyamines, pyridines and the like, the latter can be used without any diluent. However, where the nucleophilic reagent is a gas, such as ammonia or trimethylamine, an appropriate solvent therefor can be employed.

Advantageously, a wide variety of nucleophilic reagents may be employed in the present invention. Illustrative reagents are: pyridine, α-picoline, β-picoline, γ-picoline or mixtures thereof, trimethylamine, triethylamine, tri-n-propylamine, N,N-dimethylamine, aminotriacetic acid, tri-β-hydroxyethylamine, β-dimethylaminoethyl alcohol, N,N-dimethyl-o- (or m-, or p-) toluidine, N,N-dimethylbenzylamine, dimethylaniline, N-ethyl-N-methylaniline, N,N-diethylaniline, quinoline, isoquinoline, dl-nicotine, N,N-di-n-propylaniline, 6-methylquinoline, 2-phenylpyridine, N,N-dimethyl-α- (or β-) naphthylamine, N-benzyl-N-methylaniline, N-benzyl-N-ethylaniline and triethanolamine. Also contemplated are: methylamine, propylamine, hexylamine, benzylamine, iminodiacetic acid, trimethylene diamine, ammonia, hexamethylene tetramine, glycine, lycine, sodium sulfite, potassium bisulfite, sodium sulfide and equivalents thereof, mono-, di- or tri-substituted phosphines, phosphites or dithiophosphates.

Advantageously, so-grafted polymeric fibers can be uniformly dyed without prior nucleophilic reagent pretreatment with acid and direct dyes at about 75° C. to 130° C. in a solvent such as dimethylformamide. Examples of the dyes employed are the following: Calcocid Brilliant Scarlet 3 RN (Acid Red 18); Calcocid Fast Red A (Acid Red 88); Calcocid Yellow MCG (Acid Yellow 23); Calcocid Alizarin Green CGN (Acid Green 25); Calcocid Alizarin Blue SAPG (Acid Blue 45); Calcocid Red FC (Direct Red 1); Calcocid Fast Orange 2R (Direct Orange 26); Calcozine Violet N (Direct Violet 1).

Alternatively, the grafted material may initially be treated with a nucleophilic reagent whereby the fibers are rendered dyeable in standard aqueous dye baths using either an acid or a direct dye. In addition to all the dyes enumerated above, the following dyes produce extremely deep shades of true colors: Calcocid Phloxine 2G (Acid Red 1); Calcocid Green B Conc. (Acid Green 1) and Calcodur Turquoise GL (Direct Blue 86).

Similarly, the grafted fiber initially treated with a solubilized alkali metal sulfide or sulfite permits ready dyeability with basic dyestuffs. For instance, by dissolving salts such as sodium sulfite, sodium bisulfite or sodium sulfide in a solvent, such as dimethylformamide, the fiber material can be dyed with basic dyes of which the following are illustrative: Calcozine Acrylic Violet 3R, Sevron Blue 2G, Calcozine Acrylic Red 3G, Sevron Yellow R.

For a clearer understanding of the invention, the following examples are presented for purposes of illustration. They are not intended to be construed as being limitative thereof. Unless otherwise specified, the parts given are by weight.

## EXAMPLE 1

Twenty-five parts of 3 denier polypropylene tow are placed in a suitable glass ampoule reactor. The latter is attached to a high vacuum line and evacuated. One hundred parts of a mixture consisting of 47.34 parts of chloromethylstyrene, 47.34 parts of styrene and 5.32 parts of divinyl benzene are distilled into the ampoule under reduced pressure of residual gases of about $10^{-6}$ mm. Hg. The reactor is sealed off and its contents allowed to equilibrate overnight. Then the ampoule and contents are subjected to irradiation with 250 kiloelectron volts, peak value (kevp.), X-rays to a total dose of 0.27M rad at a dose rate of 1.6M rads/hr. The contents are permitted to remain sealed overnight and are then removed from the glass ampoule by breaking the latter. The fiber is washed several times with toluene, then with methanol and dried in an oven at 100° C. A weight gain of 7.6 parts indicates a graft of about 8.5% chloromethylstyrene, 13.6%

styrene and 1.5% divinyl benzene, all based on the final weight of the fiber.

About 0.5 part of the so-formed fiber which on electron microscopic examination possesses a spongy structure, is dyed with a solution of 0.005 part Calcocid Alizarin Blue SAPG in 25 parts (by volume) of dimethylformamide at 120° C. for one hour. The dyed sample is rinsed with water, then boiled in water for one hour and air-dried. The fibers are uniformly dyed to a dark blue shade.

A portion of these same dyed fibers is "potted" in polymethylmethacrylate. Several thin cross sections are next prepared by slicing the potted fibers on a microtome. Examination of the cross sections of the fibers by microscopic techniques reveals that about 75% of the fibers are dyed completely to the center. The examination further reveals that fibers which are not dyed all the way through to the center, exhibit dye penetration to at least (or greater than) two-thirds of the radius of each such fiber. In addition, no sticking temperature up to 270° C. is observed.

Another portion of the grafted, but undyed fibers is likewise "potted" and sectioned as above. These sections are examined by transmitted light in an ultraviolet microscope at wavelengths where polychloromethylstyrene absorbs strongly but where polypropylene is essentially transparent. It is observed that at least 90% to 95% of the fibers are grafted all the way to the center. Those fibers which are not grafted all the way to the center exhibit transparent center sections.

## EXAMPLE 2

Polypropylene tow (25 parts) is placed in one ampoule of a suitable apparatus consisting of two ampoules connected at their necks with a tube which is attached to a high vacuum line. In the other ampoule are added 100 parts of a mixture consisting of 40 parts of methylstyrene, 20 parts of divinyl benzene and 40 parts of chloromethylstyrene. The monomeric mixture is degassed by repeated freeze-evacuate-thaw cycles. The evacuated apparatus is sealed off and the fiber irradiated with 250 kevp. X-rays to a total dose of 1M rad at a dose rate of 1M rad/hr. During irradiation, the monomeric mixture is shielded from X-rays by one-half inch lead shield around the ampoule containing it. Thirty seconds after irradiation is terminated, the monomeric mixture is poured onto the fiber, completely immersing it, and allowed to stand overnight. The apparatus is opened, the fiber washed with toluene, then with methanol and dried in an oven at 100° C. A polypropylene-grafted fiber weight gain of 7 parts shows a 5.5% graft of the chloromethylstyrene, 14.5% graft of the methylstyrene and 2% of the divinyl benzene.

0.5 part of the grafted fiber is dyed a brilliant blue by 0.005 part Calcocid Alizarin Blue SAPG in 25 parts by volume of dimethylformamide at 120° C. for about one hour.

A sample of the original ungrafted fiber subjected to an identical dyeing procedure remained completely colorless. Further, the nongrafted fiber had a "waxy" hand.

Another portion of the fiber so-prepared is immersed in pyridine at 60° C. for thirty minutes, washed with water and several swatches of it are next dyed to deep shades in a series of standard aqueous dye baths employing either direct or acid dyes. Typical dyes so utilized are: Calcocid Brilliant Scarlet 3N (Acid Red 18), Calcocid Phloxine 2G (Acid Red 1), Calcomine Fast Orange (Direct Orange 26) Calcocid Yellow MCG (Acid Yellow 23), Calcocid Green B Conc. (Acid Green 1), Calcodur Turquoise GL (Direct Blue 86), Calcocid Alizarin Blue SAPG (Acid Blue 45), and Calcozine Violet N Conc. (Direct Violet 1).

Each of the fibers so-dyed is exposed simultaneously to heat and ultraviolet and visible light in a standard carbon arc fadeometer. Visual examination of each is next performed after 20, 40 and 80 hours. No fading is noticed after 40 hours exposure. Further, each dyed portion is rated in a fadeometer test. This is the same rating given to these specific dyes when they are dyed on wool to deep shades and exposed in the same manner.

Each of the dyed fiber samples is color-fast to washing at 160° F. with a 1% soap solution containing 0.1% sodium carbonate.

## EXAMPLE 3

This example illustrates the treatment of polypropylene powder.

One part of polypropylene powder is placed in a suitable ampoule attached to a high vacuum line. Four parts of a mixture comprising 1.5 parts of chloromethylstyrene, 1.75 parts of acrylonitrile and 0.75 part of divinyl benzene are vacuum-distilled onto the powder. The ampoule is then sealed off under a reduced pressure of about $10^{-6}$ mm. Hg and subjected to irradiation with 250 kevp. X-rays to a dose of 0.27M rad at a dose rate of 1.6M rads/hr. Polypropylene powder with a 9% graft of chloromethylstyrene, 15% graft of acrylonitrile and 2.1% graft of divinyl benzene is obtained. The grafted powder does not melt below 310° C. while the ungrafted polypropylene powder melts at about 165° C. Further, the grafted powder advantageously exhibits improved antistatic properties. Moreover, it can also be extruded in the usual fashion to form a nondiscoloring polypropylene fiber.

## EXAMPLE 4

In a suitable glass bottle, carded polypropylene fiber (15 parts), through which nitrogen has been blown for about one hour, is immersed in 160 parts of a mixture consisting of chloromethylstyrene previously purged with nitrogen, 90 parts of methylmethacrylate and 20 parts of divinyl benzene. The mixture is heated to 55° C. for one hour, while nitrogen is bubbled through it, to increase the amount of monomer imbided by the fiber during the process of swelling. The bottle containing the fiber and monomer is tightly stoppered and irradiated with 3 mev. X-rays at a dose rate of 0.4M rad/hr. to a total dose of 0.2M rad. Weight gain after extraction of the fiber with toluene at room temperature shows a 9.5% graft of the chloromethylstyrene, a 16% graft of the methylmethacrylate and a 3% graft of the divinyl benzene. The fiber is readily dyeable to deep shades in dimethylformamide or in aqueous dye baths after treatment with pyridine.

So-grafted, pyridine-treated fiber is placed in an atmosphere of air at 23° C. and 50% relative humidity for 48 hours after which it is weighed. It is then placed in an oven at 105° C., cooled and weighed again. The "percent (%) moisture regain" is defined as the maximum difference in weight observed, multiplied by 100 and divided by the "bone-dry" weight. Typical data are shown below which are to be compared with the figure of 4% for the material cited in this example.

Table I

| Material: | Percent moisture regain |
|---|---|
| Chloromethylstyrene-methylmethacrylate-divinyl benzene-grafted pyridine-treated polypropylene | 4.0 |
| Acrylan acrylic fiber | 1.7 |
| Orlon acrylic fiber | 0.9 |
| Dacron polyester fiber | 0.4 |
| Dynel acrylic fiber | 0.3 |
| Polypropylene | 0.0 |

## EXAMPLE 5

0.5 part of polypropylene fiber, prepared in accordance with Example 4 above, is heated at 100° C. for one hour in a mixture of 500 parts of dimethylformamide and 1 part of sodium sulfite. The fiber samples are washed with water and dried at 100° C. Portions of each are then

dyed in aqueous solutions of each of the following basic dyes:

(a) Calcozine Acrylic Red 3G,
(b) Calcozine Acrylic Violet 3R,
(c) Sevron Blue 2G (C.I. Basic Blue 22),
(d) Sevron Yellow R (C.I. Basic Yellow 11).

Dyeability is markedly improved over controls which consist of ungrafted, untreated polypropylene fiber and grafted but not treated polypropylene fiber.

Similar results are obtained when sodium bisulfite or sodium sulfide is substituted in lieu of the sodium sulfite in the above example.

We claim:

**1.** A process for preparing a dyeable, preformed, colorless, heat-stable polypropylene fiber of good tensile strength, which comprises the steps of: subjecting preformed polypropylene fibers in the solid state and in the substantial absence of oxygen environment to high energy ionizing radiation at a temperature between about 70° C. and 150° C. to provide a dose between about 5,000 rads and about 20,000,000 rads while contacting the irradiated fibers with a mixture of monomers containing (1) chloromethylstyrene monomer, (2) a polymerizable vinyl monomer selected from the group consisting of styrene, methylstyrene, acrylonitrile, methacrylic acid and methylmethacrylate, and (3) a cross-linking agent selected from the class consisting of divinyl benzene, bismethylene acrylamide, triallyl cyanurate, tetraallyl melamine, hexaallyl melamine and diallyl sebacate, present in amounts sufficient to impart an overall weight increase from (1) 1% to 10%, (2) 10% to 30, and (3) 1% to 10%, respectively, by weight of the fiber, and recovering a chloromethylstyrene-vinyl-grafted polymeric fiber.

**2.** A process according to claim **1**, in which the ionizing radiation consists of high-energy electrons.

**3.** A process according to claim **1**, wherein the monomer is provided at a temperature between about 40° C. and 120° C.

**4.** A process according to claim **1**, in which the irradiation is supplied by gamma-rays.

**5.** A process according to claim **1**, in which the irradiation is performed by means of particulate $\beta$-radiation.

**6.** A process according to claim **1**, in which the irradiation is carried out by means of X-rays.

**7.** A process according to claim **1**, in which the graft polymer is dyed in a nonaqueous medium.

**8.** A process according to claim **1**, in which the graft polymer is dyed in dimethyl formamide.

**9.** A process according to claim **1**, in which the graft polymer is first subjected to treatment with a nucleophilic reagent and the so-modified polymer is thereafter dyed in an aqueous medium.

**10.** A process according to claim **9**, in which the nucleophilic reagent is selected from the class consisting of pyridine, $\alpha$-picoline, $\beta$-picoline, a mixture of $\alpha$-, $\beta$-, $\gamma$-picolines, trimethylamine and aminotriacetic acid.

**11.** A process according to claim **10**, in which the nucleophilic reagent is pyridine.

**12.** A process according to claim **10**, in which the nucleophilic reagent is $\alpha$-picoline.

**13.** A process according to claim **10**, in which the nucleophilic reagent is $\beta$-picoline.

**14.** A process according to claim **10**, in which the nucleophilic reagent is a mixture of $\alpha$-, $\beta$-, $\gamma$-picolines.

**15.** A process according to claim **10**, in which the nucleophilic reagent is trimethylamine.

**16.** A process according to claim **10**, in which the nucleophilic reagent is aminotriacetic acid.

**17.** As a novel fiber, a light-stable, heat-stable colorless, cross-linked chloromethylstyrene-vinyl-grafted, preformed polypropylene fiber capable of being uniformly dyed substantially to the center of said fiber and possessing good tensile strength, a spongy structure and devoid of a sticking temperature up to at least 270° C. produced by the process of claim **1**.

**18.** The novel fiber according to claim **17**, in which the average molecular weight of the polypropylene falls within the range of from about 100,000 to about 1,000,000.

**19.** As a novel fiber, a heat-stable, deeply-dyed, cross-linked chloromethylstyrene-vinyl-grafted polypropylene fiber possessing good tensile strength, devoid of a sticking temperature up to at least 270° C., good moisture regain, antistatic and color wash-fastness properties produced by the process of claim **7**.

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