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ARTICLES HAVING IMPROVED TINCTORIAL PROPERTIES AND METHOD OF PREPARING SAME

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23 Claims. (Cl. 8—115.5)

The present invention relates to the improvement of the tinctorial characetristics of textile fibres, films, tapes, shaped articles and the like, obtained by extrusion of mixtures of polyolefins consisting essentially of isotactic macromolecules and basic substances acting as tinctorial modifiers, with or without other materials such as stabilizers, solid dispersing agents, opacifiers, dyes and the like.

More particularly, the present invention relates to the treatment of fibres and the like with mono- and/or bifunctional derivatives obtained by the reaction of epichlorohydrin with long chain aliphatic amines or with aromatic or heterocyclic amines in order to improve dye receptivity, and to obtain a good color fastness and improved hand characteristics in the resulting textile fibres.

Textile fibres obtained from mixtures of synthetic polymers and tinctorial modifiers of a basic nature have a good receptivity to dyes, but are disadvantageous in that the basic compounds mixed with the olefin polymer is somewhat water soluble. Moreover, the tinctorial modifier shows a tendency to migrate out from the fibres, thus causing a "greasiness" in the manufactured articles ultimately obtained.

It is an object of the present invention to eliminate the aforementioned inconveniences by rendering the tinctorial modifier water insoluble and preventing it from migrating out of the fibre.

We have now surprisingly found that the water solubilization of the basic substance previously incorporated in the polymer and its removal from such polymer can be avoided by treating the foregoing fibres with N-glycidyl or N,N'-diglycidyl derivatives of aliphatic, aromatic and heterocyclic amines, or with the mono- or di-chlorohydroxypropyl derivatives of aliphatic, aromatic and heterocyclic amines.

The treatment of the present invention makes it possible to reduce the amount of tinctorial modifiers incorporated in the polyolefin, since the treatment with the nitrogen compounds according to the invention makes it possible to introduce into the fibre that amount of nitrogen required to increase the dyeability of the polyolefin with acid dyes.

Suitable compounds which can be used according to the present invention include N-mono-glycidyl derivatives and N-di-glycidyl derivatives of n-dodecylamine and of n-octadecylamine, N-mono- and di-chlorohydroxypropyl derivatives of n-dodecylamine and octadecylamine, N-glycidylpiperazine, N,N'-diglycidylpiperazine, N-chlorohydroxypropylpiperazine, and N,N'-di(chlorohydroxypropyl)piperazine.

The N-mono- and diglycidyl derivatives of primary C_{12}–C_{18} aliphatic amines and of piperazine as well as the mono-chlorohydroxypropyl and di-(chlorohydroxypropyl) derivatives are applied from solutions or dispersions in water or in an organic solvent or in the anhydrous state.

The application of the foregoing compounds can be carried out before or after stretching of the fibres. The duration of the treatment may vary from a few seconds to 3 hours, at a temperature of from about room temperature to 10° C. below the softening point of the base polymer.

Textile fibres which are to be subjected to the treatment of the present invention consist essentially of at least 75% of a polyolefin, more particularly polypropylene consisting essentially of isotactic macromolecules and obtained by stereospecific catalysis of propylene, and from about 1 to 25% of a tinctorial modifier.

The tinctorial modifiers (basic nitrogen compounds) used for preparing dyeable textile fibres may be amines or imines of the polyalkylenimine type, or may comprise a nitrogen polycondensate of epichlorohydrin, having a specific viscosity, determined at 25° C. in 1% isopropanol solutions, comprised between 0.1 and 0.7.

The mixtures, after granulation or simple sintering, are extruded in a melt spinning device using spinnerets having a length/diameter ratio greater than 1.

The granulation and spinning are carried out by operating in the absence of oxygen, and preferably under an inert gas (e.g., nitrogen).

Spinning of the mixtures can conveniently be carried out in the presence of a small amount of a solid dispersing agent which facilitates the homogeneous dispersion of the basic nitrogen compound in the molten polymer mass. The dispersing agent is desirably one of the following materials: octyl and/or stearyl alcohols, stearic acid, benzoin, furoin, vinyl stearate, mono-, di- and tri-stearic esters of glycerol, monoethanolamine stearate, stearamide, N-diethanol-lauramide, C_6–C_{30} aliphatic amines, condensation products of ethylene oxide with amines of phenols, polystearamide, polyacrylic acid, polystyrene, styrene copolymers, terpene polymers, and the like.

During the mixing, stabilizers, opacifiers, and organic or inorganic pigments can, if desired, be added to the polyolefin in addition to the foregoing nitrogen compounds.

The fibres, after spinning, are subjected to a stretching process, with stretching ratios of from about 1:2 to 1:10, at temperatures of from about 80 to 150° C., in stretching devices heated with hot air or steam or with a similar fluid, or provided with a heating plate.

The fibres thus obtained can be subjected to a dimensional stabilization treatment under conditions of free or hindered shrinking from about 80–160° C.

The fibres obtained by extrusion of the mixtures of the present invention can be mono- or plurifilaments and can be used for preparing bulk yarns or bulk staple fibres.

According to the present invention the fibres subjected to the treatment with the aforementioned mono- and diglycidyl derivatives and/or mono- and di-(chlorohydroxypropyl) derivatives exhibit a remarkable receptivity for acid dyes, metallized dyes, and disperse dyes. Such fibres also exhibit a good affinity for basic and vat dyes, exhibit superior hand characteristics, and show particularly solid colors. Moreover the fibres obtained according to the present invention show an increased stability with respect to light.

The control dyeing tests were carried out for 1 hour and half at the boiling point, in baths containing 2.5% of dye by weight of the fibre, with a fibre/bath ratio of 1:40.

Dyeing with acid and metallized dyes was carried out in the presence of 3% ammonium acetate (calculated on the fibre weight) and of 1% of a surface-active agent, namely, the condensation product of 6–20 mols of ethylene oxide with 1 mol of an alkylphenol such as p-tert. octylphenol, nonylphenol and the like.

After 30 minutes from the commencement of boiling, 2% (calculated on the fibre weight) of a 20% acetic acid solution was added in order to improve the exhaustion of the baths.

After dyeing, the fibres were rinsed with running water, and the resulting fibres showed intense colors with acid dyes, metallized dyes, and disperse dyes.

The color fastness to light, washing and rubbing is very satisfactory.

The process of the present invention can be also used for improving the tinctorial characteristics and color fastness of various other synthetic fibres, such as the fibres obtained from polyamides, polyesters, acrylic polymers and copolymers, vinyl polymers and copolymers, each in admixture with basic nitrogen substances.

Variations and modifications can of course be made without departing from the spirit and scope of the invention.

The following examples will further illustrate the invention.

EXAMPLE 1

A yarn is prepared by extruding a mixture of: 9.6 kg. of polypropylene having an intrinsic viscosity [η] of 1.58 (measured in tetrahydronaphthalene at 135° C.), an ash content of 0.012%, and a residue after heptane extraction of 96.2%; 0.4 kg. of a basic nitrogen polycondensate obtained by reacting 1.30 moles of epichlorohydrin with 0.3 mol of octadecylamine and 1 mole of piperazine, and having a specific viscosity [η_{sp}] of 0.32 (determined in 1% isopropanol solution at 25° C).

The mix is spun and then treated with diglycidyloctadecylamine under the operating conditions reported in the table hereinafter.

EXAMPLE 2

A yarn is prepared by extruding a mixture of: 9.6 kg. of polypropylene having an intrinsic viscosity [η] of 1.58 (determined in tetraline at 135° C.), an ash content of 0.012% and a residue after heptane extraction of 97.2%; 0.4 kg. of a basic nitrogen polycondensate obtained by reacting of 0.65 mol of epichlorohydrin with 0.3 mol of dodecylamine and 0.35 mol of piperazine, and having a specific viscosity [η_{sp}] of 0.27 (determined in 1% isopropanol solution at 25° C.).

The mix is spun and then treated with diglycidyl piperazine under the operative conditions reported in the table.

EXAMPLE 3

A yarn is prepared by extruding a mixture of: 9.8 kg. of polypropylene having an intrinsic viscoisty [η] of 1.62 (measured in tetraline at 135° C.), an ash content of 0.015%, and a residue after heptane extraction of 95.6%; 0.4 kg. of a basic nitrogen polycondensate obtained by reaction of 1 mole of diglycidylpiperazine with 1 mole of piperazine, and having a specific viscosity [η_{sp}] of 0.29 (determined in 1% isopropanol solution at 25° C.).

The mix is spun and then treated with di(chlorohydroxypropyl)dodecylamine under the operative conditions reported in the table.

EXAMPLE 4

A yarn is prepared by extruding a mixture of: 9.6 kg. of polypropylene having an intrinsic viscosity [η] of 1.62 (measured in tetraline at 135° C.), an ash content of 0.015%, and a residue after heptane extraction of 95.6%; 0.4 of a basic nitrogen polycondensate obtained by reacting 1.3 moles of epichlorohydrin with 0.3 mole of octadecylamine and 1 mole of piperazine, and having a specific viscosity [η_{sp}] of 0.32 (determined in 1% isopropanol solution at 25° C.).

The mix is spun and then treated with diglycidylpiperazine under the operative conditions reported in the table.

EXAMPLE 5

A yarn is prepared by extruding a mixture obtained from 9.6 kg. of polypropylene having an intrinsic viscosity of 1.62 (measured in tetraline at 135° C.), an ash content of 0.015% and a residue after heptane extraction of 95.6%; and 0.4 kg. of poly-2-vinylpyridine prepared with stereospecific catalysts, and having an intrinsic viscosity [η] of 0.45 (determined in dimethylformamide at 30° C.).

The mix is spun and then treated with diglycidylpiperazine under the operative conditions reported in the table.

Table

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5
Spinning conditions:					
Screw temperature	250 °C	250° C	250° C	250° C	250° C.
Head temperature	250° C	250° C	250° C	250° C	250° C.
Spinneret temperature	240° C	240° C	240° C	240° C	240° C.
Spinneret type	60/0.8×16 mm.	60/0.8×16 mm.	60/0.8×16 mm.	60/0.8×16 mm.	60/0.8×16 mm.
Max. pressure (kg./cm.²)	75	68	105	81	78.
Winding speed (m./minute)	300	300	300	300	300.
Stretching conditions:					
Temperature	130° C	130° C	130° C	130° C	130° C.
Medium	Steam	Steam	Steam	Steam	Steam.
Stretching ratio	1:5.3	1:5.3	1:5.3	1:5.3	1:5.3.
Finishing:					
Treatment for 5 minutes with a 5% methanol solution of di(chlorohydroxypropyl)dodecylamine (temperature).			25° C		
Treatment for 5 minutes with a 5% methanolic solution of diglycidyloctadecylamine(temperature).	25° C				
Treatment for 5 minutes with a 5% methanolic solution of diglycidylpiperazine(temperature).		25° C		25° C	50° C.
Characteristics of the stretched fibre:					
Tenacity (g./den.)	5.1	5.5	5.3	5.25	5.3.
Elongation (percent)	25	22	26	24.5	27.
Dyeing with acid dyes:					
Alizarine yellow 2G (C.I. mordant yellow 1).	Good	Good	Good	Good	Good.
Wool red B (C.I. acid red 115)	do	do	do	do	Do.
Alizarine red S (C.I. mordant red 3)	do	do	do	do	Do.
Alizarine blue SE (C.I. acid blue 43)	do	do	do	do	Do.
Acid black JVS (C.I. acid black 1)	do	do	do	do	Do.
Dyeing with metallized dyes:					
Lanasyn yellow GLN (C.I. acid yellow 112).	do	do	do	do	Do.
Lanasyn red 2GL (C.I. acid red 216)	do	do	do	do	Do.
Lanasyn brown 3RL (C.I. acid brown 30).	do	do	do	do	Do.
Dyeing with disperse dyes:					
Setacyl yellow 3G (C.I. disperse yellow 20).	do	do	do	do	Do.
Cibacet scarlet BR (C.I. disperse red 18).	do	do	do	do	Do.
Brilliant setacyl blue BG (C.I. disperse blue).	do	do	do	do	Do.
Color fastness with acid dyes	do	do	do	do	Do.
Color fastness with metallized dyes	do	do	do	do	Do.
Color fastness with disperse dyes	do	do	do	do	Do.

Having thus described our invention, what we desire to secure and claim by Letters Patent is:

1. A process for rendering more dye receptive textile fibres obtained by the extrusion of a mixture of a synthetic polymer with a basic nitrogen substance which functions as a tinctorial modifier, said process comprising treating said fibres with a compound selected from the group consisting of monoglycidyl amines, diglycidyl amines, chlorohydroxypropyl amines and di(chlorohydroxypropyl) amines, said amines being selected from the group consisting of aliphatic, aromatic, and heterocyclic amines.

2. The process of claim 1 wherein said synthetic polymer constitutes at least 75% of said mixture.

3. The process of claim 1 wherein said polymer is a poly-alpha olefin consisting essentially of isotactic macromolecules.

4. The process of claim 3 wherein said polyalpha-olefin is polypropylene consisting essentially of isotactic macromolecules.

5. The process of claim 2 wherein the amount of basic nitrogen substance in said mixture is from about 1 to 25% by weight of said mixture.

6. The process of claim 5 wherein said basic nitrogen substitute is an amine.

7. The process of claim 5 wherein said basic nitrogen substitute is an amine.

8. The process of claim 5 wherein said basic nitrogen substance is a polyalkylenimine.

9. The process of claim 5 wherein said basic nitrogen substance is a basic nitrogen polycondensate of epichlorohydrin.

10. The process of claim 9 wherein said basic nitrogen polycondensate is obtained by the reaction of 1 mole of epichlorohydrin with an amount of n-octadecylamine and piperazine totalling 1 mole.

11. The process of claim 9 wherein said nitrogen polycondensate is obtained by the reaction of 1 mole of epichlorohydrin and an amount of n-dodecylamine and piperazine totalling 1 mole.

12. The process of claim 1 wherein said treatment is carried out for from about a few seconds to 3 hours, at a temperature of from about room temperature to 10° C. below the softening point of the synthetic polymer.

13. The process of claim 1 wherein said treatment is carried out continuously.

14. The process of claim 1 wherein said treatment is carried out batchwise.

15. The process of claim 1 wherein said treatment is effected before stretching of the fibres.

16. The process of claim 1 wherein said treatment is effected after stretching of the fibres.

17. The process of claim 1 wherein a glycidyl-n-dodecylamine is employed.

18. The process of claim 1 wherein a glycidyl-n-octadecylamine is employed.

19. The process of claim 1 wherein a glycidylpiperazine is employed.

20. Textile fibres in the form of filaments, staple fibres, yarns, films, tapes, and other shaped articles having a remarkable receptivity to dyes, obtained by the process of claim 1.

21. The process of claim 1 wherein a chlorohydroxypropyl-n-dodecylamine is employed.

22. The process of claim 1 wherein a chlorohydroxypropyl-n-octadecylamine is employed.

23. The process of claim 1 wherein a chlorohydroxypropylpiperazine is employed.

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NORMAN G. TORCHIN, *Primary Examiner.*

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 13, for "characetristics" read -- characteristics --; column 5, line 26, for "amine" read -- imine --.

Signed and sealed this 21st day of June 1966.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents