POLYOLEFIN FIBRES HAVING IMPROVED TENC- TIONAL CHARACTERISTICS AND PROCESS FOR PREPARING THE SAME

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16 Claims. (Cl. 8—115.5)

The present invention relates to the preparation of dyed polyolefin fibres and, more particularly, to a process for improving the textural characteristics of such fibres.

Certain recent patents have described various types of fibres consisting of olefin polymers obtained under low pressure with the aid of stereospecific catalysts. Such polyolefin fibres have many advantageous characteristics. However, these fibres hitherto have exhibited poor dyeability characteristics.

The chief object of the present invention is the treatment of polyolefin fibres to render them easily dyed with acid or basic dyes. Additional objects will become apparent hereinafter.

We have made the surprising discovery that the dye receptivity of fibres made from polymers of mono-olefin hydrocarbons increases substantially if the fibres are subjected to a preliminary treatment with phosgene (carbonyl chloride).

According to one aspect of our invention the treatment with phosgene may be carried out directly on the polyolefin fibre, either in gaseous medium in liquefied phosgene, or in suspension in another liquid. The liquid may be organic, e.g. cyclohexane, or inorganic, e.g. sulphuric acid. Under the operative conditions of the phosgenation treatment, the liquid used should not dissolve the fibre polymer. The fibre may be employed in the form of staple, yarn or fabric.

The treatment with phosgene does not alter the physical characteristics of the fibres, but does cause a structure modification resulting in a certain variation of the infrared spectrum. The fibres thus treated acquire high dyability with basic and microsotyl dyes.

We have also found that if the fibres treated with phosgene are subjected, before dyeing, to washing with water or with aqueous solutions of organic or inorganic acids or bases, particularly good textile results are obtained. Moreover, the polyolefin fibres treated with phosgene may be subjected to an amination treatment in order to increase the affinity to acid dyes.

In accordance with another aspect of our invention, we have found that the conditions of the phosgenation treatment may be very mild provided that initially hydroperoxy groups have been introduced, into the polyolefin fibre, e.g. as by treatment of the fibre in an oven at 70-80°C.

According to another aspect of our invention, before extrusion the polyolefin is mixed with a polyhydroxyl compound or with a compound capable of becoming such during the extrusion operation. The mix is then extruded and the fibres are treated with carbonyl chloride. Subsequent treatment with amines imparts to the fibres high dyability with acid dyes.

If polyhydroxy compound is mixed with the polyolefin prior to extrusion, the polyhydroxy compound should have the following characteristics: be dispersible in the polyolefin in the molten state; have a sufficiently high melting point, i.e., not much higher than the melting point of the polyolefin yet higher than the extrusion temperature; have thermal stability and low vapor pressure at the extrusion temperature. Suitable polyhydroxy compounds include aliphatic or aromatic epoxy resins or phenol-formaldehyde condensation resins of the "novolac" type.

The epoxy resins are preferably of low molecular weight. Hydroxyl groups are formed by the opening of the epoxy ring.

where n is an integer from about 2 to 10.

The polyhydroxy compound reacts with the carbonyl chloride (phosgene) as shown by the following equation:

\[ R-OH+COCl_2 \rightarrow ROCOCI+HCl \]

where R is the residue of the polyhydroxy compound, which residue also contains hydroxy groups. The ROCCI compound thus obtained then reacts with an amine, either in the presence or absence of water.

The amination may be carried out with compounds containing amine or imine groups. Suitable amines include ethylenediamine, trimethylene diamine, diethylene trimine, tetraethylene pentamine, hexamethylene diamine, etc. Suitable imines include alkylnamine, such as ethylene amine, etc.

According to an alternative procedure of our invention, the reaction with phosgene can be effected directly on the polyhydroxy compound, before mixing it with the polyolefin. (In this case, of course, the phosgenation is carried out before extruding the polyolefin-polyhydroxy compound mix.)

It will be seen, therefore, that the reaction of carbonyl chloride with the fibre and the amination may be carried out either before or after stretching the fibre.

The amination of the phosgenated fibres is preferably carried out by treating the fibres with boiling aqueous solutions of amines for a time that may vary from a few seconds to two or three hours, depending on the reactivity of the amine used.

The polyhydroxy compounds (or the reaction products thereof with carbonyl chloride) are added to the polyolefin, before spinning, in the ratio of between about 1 to 20% by weight of the mix.

The reaction of carbonyl chloride with the fibre takes place by exposure of the fibre for about 15 to 30 minutes to a stream of COCl₂. For phosgenation of the polyhydroxy compound, this may be carried out in homogeneous phase (e.g., solution in organic solvents) or in heterogeneous phase by passing for 30 to 60 minutes a stream of COCl₂ through the solution. The dyes suitable for dyeing the fibres according to this feature of the invention are acid, basic or acetic dyes. The following examples will further illustrate our invention. Although these examples are directed to two preferred polymers, i.e., polypropylene and polyethylene, it will be understood that our invention is also applicable to other olefin polymers, such as e.g., polybutene.

As will be seen from the following examples, the application of the above process steps to fibres obtained from polypropylene consisting prevalingly of isotactic
3,116,966

macromolecules, results in the production of fibres possessing improved textural characteristics. The term “intertext” was originated by G. Natta and, as known to the art following Natta, identifies the structure described in "The Journal of Polymer Science," vol. XVI, p. 145-154, April 1955, and in U.S. Patent 2,882,263.

All parts are by weight unless otherwise indicated.

**Example 1**

10 g. polypropylene staple are introduced into an evacuated 1-litre flask. Phosgene is introduced under ordinary pressure. The flask is maintained at about 50° C. for 16 hours, with the introduction of additional phosgene intermittently. The flask is then purged with air at room temperature. The contents are washed with water until no gas that was mechanically retained has been completely removed. The fibre is dyed with Auramine O (Color Index No. 41,000), thereby obtaining an intense brilliant yellow color presenting good fastness.

**Example 2**

10 g. polypropylene staple are immersed in 200 ml. of cyclohexane in a tube provided with a porous diaphragm. Phosgene is passed through at 25° C. for 10 hours. After treatment with air, the fibre is removed from the solvent. It is then washed, first with water acidified with hydrochloric acid, and then with tap water. The fibre is then dried. The fibre is dyed with Brilliant Green (Color Index No. 42,040), thereby obtaining a green color presenting good fastness.

**Example 3**

10 g. polypropylene fabric are treated as described in Example 1, except that the flask is maintained at 25° C. for 18 hours. The fabric is washed with a 0.12% sodium hydroxide solution and then with water. The fabric is dyed with Astrazon Orange G (Color Index 48,035), thereby obtaining a color presenting good general fastness.

**Example 4**

A polypropylene yarn is passed continuously in liquid phosgene at 0° C. with a residence time of about half an hour. The yarn is freed of residual gas by washing, first with dilute aqueous ammonia and then with tap water. The yarn is dyed in a bath of Methyline Blue (Color Index No. 52,015), thereby obtaining a stable blue color.

**Example 5**

10 g. polypropylene fabric are treated with stirring, in a tube provided with a porous diaphragm, with phosgene for 6 hours at 20° C. in 60% sulfuric acid. After removal of the acid, the fabric is rinsed in water and washed, first with a sodium carbonate solution and then with tap water. The fabric is printed with Rhodamine B (Color Index No. 45,170), thereby obtaining a brilliant stable color having good general fastness.

**Example 6**

A mix of 95 kg. polypropylene (having an intrinsic viscosity of 1.09 determined in tetrahydroxynaphthalene at 135° C., a residue after heptane extraction of 86.2%, and an ash content of 0.028%, and 5 kg. epoxy resin, obtained from the condensation of epichlorohydrin with "bis-phenol-A") is prepared at room temperature in Werner type mixer. The mix is spun under the following conditions:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spinnernet temperature</td>
<td>210</td>
</tr>
<tr>
<td>Spinning head temperature</td>
<td>220</td>
</tr>
<tr>
<td>Screw temperature</td>
<td>260</td>
</tr>
</tbody>
</table>

The yarn obtained can be worked, e.g., as described in the U.S. patent application 727,398, so as to obtain a bulky yarn. Such yarn skeins or normal yarn skeins are introduced into a reactor and are subjected to a stream of COCl₂ at room temperature for about 20 minutes. They are then washed with water and introduced into boiling aqueous solutions of the following amines for the times indicated:

<table>
<thead>
<tr>
<th>Amine</th>
<th>Time (Minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyline diamine (10% solution)</td>
<td>10</td>
</tr>
<tr>
<td>Ethylene imine (3% solution)</td>
<td>20</td>
</tr>
<tr>
<td>Tetraethylen pentamine (anionrous)</td>
<td>30</td>
</tr>
</tbody>
</table>

When dyed with acid dyes, the fibres give colors with good intensity and fastness. The same fibres, treated with phosgene but not with amines or imines, present good reactivity to basic dyes such as Deterlina Brilliant Yellow 2GL, Astrazon Yellow 3G, Sevron Red 4GL, Astrazon Red 6B, Basic Fuchsin, Astrazon Blue G, Sevron Blue L, Crystals Malachite Green, with which they give intense colors having rather good fastness under wet conditions. They can also be dyed (before or after amination) with dispersed acetate dyes such as Setyl Yellow 5G, Setacyl Yellow 3G, Aceoquinone Scarlet N, Cibacet Scarlet EB, Aceoquinone Blue RHO.

**Example 7**

A mix of 90 kg. polypropylene (having an intrinsic viscosity of 1.28, a residue after heptane extraction of 84.2%, and an ash content of 0.02%) and 10 kg. epoxy resin, obtained from the condensation of epichlorohydrin with "bis-phenol-A" is prepared at room temperature in a Werner type mixer. This mix is spun under the following conditions:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spinnernet temperature</td>
<td>200</td>
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<tr>
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<td>210</td>
</tr>
<tr>
<td>Screw temperature</td>
<td>260</td>
</tr>
</tbody>
</table>

The fibres obtained can be worked, e.g., as described in Italian Patent 579,116, so as to obtain a bulky yarn. The yarn skeins (so worked or not) are phosphated at room temperature for 30 minutes as in the preceding example. They are then washed with water and then immersed for 30 minutes in a boiling aqueous ethylene diamine solution (80%). The fibres thus obtained are dyed with the following acid dyes for wool:

<table>
<thead>
<tr>
<th>Dye</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid Yellow 2G</td>
<td>Yellow</td>
</tr>
<tr>
<td>Novamina Red B</td>
<td>Red</td>
</tr>
<tr>
<td>Alizarine Blue ACF</td>
<td>Blue</td>
</tr>
</tbody>
</table>

The colors obtained are intense and solid. The same fibres can be dyed either before or after amination with the dyes of Example 6.

**Example 8**

An epoxy resin, obtained from the condensation of epichlorohydrin with ethylene glycol and having an average molecular weight of 300, is dissolved in tetrahydrofurane (30% solution). COCl₂ is bubbled through this solution for 15 minutes. The solvent is evaporated and the phosphated epoxy resin is mixed with polypropylene (having an intrinsic viscosity of 1.23, a residue after heptane extraction of 83.6% and an ash content of 0.20%), in the proportion of 10% of the mix. 100 g. of this mix are spun in a melt spinning device at an extrusion temperature of about 200° C. under a pressure of 3 kg./cm.². The fibres obtained are treated with amine as described in Example 7. The fibres give intense and solid dyes with the following dyes:

<table>
<thead>
<tr>
<th>Dye</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid Yellow 2G</td>
<td>Yellow</td>
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<tr>
<td>Novamina Red B</td>
<td>Red</td>
</tr>
<tr>
<td>Alizarine Blue ACF</td>
<td>Blue</td>
</tr>
</tbody>
</table>

**Example 9**

A mix (100 g.) is prepared consisting of 90% polypropylene (having an intrinsic viscosity of 1.09, a residue after heptane extraction of 86.2%, and an ash content of...
0.028%) and 10% of a phenol-formaldehyde condensation resin having the following general formula:

\[
\text{OH} \quad \text{CH}_2 \quad \text{OH} \quad \text{CH}_2 \quad \text{OH} \quad \text{CH}_2 \quad \text{OH} \quad \text{CH}_2 \quad \text{OH}
\]

This mix is spun in a melt spinning device at the extrusion temperature of about 250°C. under a pressure of about 250°C. under a pressure of 4.5 kg/cm². The fibres obtained are treated with phosgene and then with amine as described in Example 7. The fibres give intense and solid colors with the dyes of Example 6 and also with the following dyes:

- Solid Yellow 2G
- Novacine Red B
- Alizarine Blue SE
- Alizarine Blue AGF

**Example 10**

A mix (100 g.) is prepared consisting of 90% polypropylene (having an intrinsic viscosity of 1.28, a residue after heptane extraction of 94.2%, and an ash content of 0.02%) and 10 g. epoxy resin obtained from the condensation of epichlorohydrin and hydroquinone having an average molecular weight of 800. This mix is spun in a melt spinning device at an extrusion temperature of about 230°C. under a pressure of 4.5 kg/cm². The fibres obtained are treated with phosgene and then with amine as described in Example 7. They are then stretched and dyed with the following dyes, thereby obtaining intense and solid colors:

- Solid Yellow EG
- Wool Red B
- Alizarine Blue SE

The same fibres can be dyed, before or after amination, with the dyes of Example 6, with equally good results.

**Example 11**

10 g. polypropylene staple are treated with phosgene as in Example 5. After removal of the acid, the staple is washed with cold water until it is neutral and is then maintained at about 20°C. for about 6 hours in a 30% aqueous monochloroamine solution. The fibre, after thorough washing with water, is dyed with Brilliant Green (Colour Index No. 42,040) thus obtaining an intense dark green color.

**Example 12**

10 g. polyethylene yarn are treated with phosgene for 6 hours at 20°C. in 500 g. 98% sulfuric acid. It is then washed with cold water until it is neutral, and is treated with a 30% monochloroamine solution at about 20°C. for about 6 hours. After washing, the yarn is dyed with the following dyes, thereby obtaining very intense colors:

- Brilliant Green (C.I. No. 42,040)
- Rhodamine B (C.I. No. 45,170)
- Astrazon Orange G (C.I. No. 48,035)
- Auramine O (C.I. No. 41,000)

Variations can, of course, be made without departing from the spirit of our invention.

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

1. A process for preparing fibres from polypropylene containing isotactic macromolecules, which fibres are particularly receptive to dyes, comprising treating said fibres with phosgene.
2. A process according to claim 1, wherein the phosgene is in gaseous form.
3. A process according to claim 1, wherein the phosgenation treatment is carried out with the fibres in suspension in an organic liquid.
4. A process according to claim 1, wherein the phosgenation treatment is carried out with the fibres in suspension in a liquid inorganic medium.
5. A process of claim 1, wherein the phosgenation treatment is carried out with liquid phosgene.
6. A process according to claim 1, wherein the treatment with phosgene is followed by washing with water.
7. The process of claim 6, wherein the water has been acidified.
8. The process of claim 6, wherein the water has been treated with an alkali.
9. The process of claim 1 wherein the starting polypropylene is mixed, before extrusion, with a polyhydroyxyl compound selected from the group consisting of the condensation product of epichlorohydrin with a phenol, the condensation product of epichlorohydrin with a polyhydric alcohol, and the condensation product of formaldehyde with a phenol, and wherein the mixture is extruded to form fibres, and these fibres are subjected to a treatment with phosgene.
10. The process of claim 9 wherein the fibres are subjected to amination by contact with a member selected from the group consisting of amines and iminies.
11. The process of claim 1, wherein the fibres are subjected to amination by contact with a member selected from the group consisting of amines and iminies.
12. The process of claim 11, wherein the amine is an aliphatic amine.
13. A process for preparing fibres from polypropylene containing isotactic macromolecules, which fibres are particularly receptive to dyes, this process comprising treating with phosgene a polyhydroyxyl compound selected from a group consisting of the condensation product of epichlorohydrin with a phenol, the condensation product of epichlorohydrin with a polyhydric alcohol, and the novolac condensation product of formaldehyde with a phenol, mixing the thus treated polyhydroyxyl compound with the polypropylene, and extruding the mixture.
14. The process of claim 13, wherein the polyhydroyxyl compound in the composition is from about 80% to 99% and the polyhydroyxyl compound is from about 1% to 20% of the composition.
15. The process of claim 13, wherein the fibres are subjected to amination by contact with a member selected from the group consisting of amines and iminies.
16. The product of the process of claim 1.

**References** Cited in the file of this patent

**UNITED STATES PATENTS**

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,116,966

January 7, 1964

Ubaldino Riboni et al.

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 5, lines 10 and 11, strike out "under a pressure of about 250° C."

Signed and sealed this 26th day of May 1964.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents