

1

2

3,383,161

**PROCESS FOR IMPROVING DYEABILITY OF THE FIBRES AND SHAPED ARTICLES OF POLYPROPYLENE**

Hiroshiro Kimura, Akio Koshimo, and Hirohisa Nara, Uji-shi, and Shunichi Fukunaga, Kyoto-shi, Japan, assignors to Nippon Rayon Co., Ltd., Kyoto-fu, Japan No Drawing. Filed July 16, 1964, Ser. No. 383,218 Claims priority, application Japan, July 17, 1963, 38/36,262

3 Claims. (Cl. 8—100)

**ABSTRACT OF THE DISCLOSURE**

A process for improving the dyeable of polypropylene by blending the polypropylene with a bisamide and then treating the blended polypropylene with halides of acetic acid, hydrogen halides or iodine, and then treating with at least one of the aliphatic amines.

The present invention relates to a process for improving dyeability of the fibres and the shaped articles of polypropylene. More particularly, this invention relates to a process for improving the dyeability of polypropylene fibres and the shaped articles blended with bisamide compounds of low molecular weight, treated with at least one compound selected from the group consisting of the halides of acetic acid, hydrogen halides and iodine, and then treated with aliphatic amine compounds.

Although the fibers and the shaped articles of polypropylene have good mechanical properties, it is difficult to dye them satisfactorily by using conventional dyestuffs and dyeing methods. The fibres and the shaped articles formed of propylene polymer have little affinity for dyestuffs because of the chemical and structural characteristics.

To improve the dyeability of polypropylene, many methods have been attempted, for example, as by grafting polypropylene with the compound having good affinity for dyestuffs, by blending polypropylene with resins having good affinity for dyestuffs, or by the adoption of chemical treatment to polypropylene, such as a sulfonation, a chlorination. In general, graft polymerization is not only difficult in the process, but also the reaction could not be homogeneously achieved. When polypropylene is blended with other resins having good affinity for dyestuffs, however, it shows bad compatibility and the obtained materials become opaque. Moreover there are many troubles in spinning, drawing or shaping process. When the fibres produced of polypropylene are subjected to merely the chemical treatments, they are dyed in a pale shade. And if the fibres are subjected to the chemical treatment under the severe conditions for the purpose of dyeing them in a deep shade, the mechanical properties of the fibres drop remarkably.

It is the object of the present invention to provide a process for improving dyeability of the fibres and the shaped articles of polypropylene which has not the above-mentioned defects.

According to the present invention, there is provided a process for improving dyeability of the fibres and the shaped articles of polypropylene characterized in that polypropylene is blended with bisamide compounds of having high hydrophobicity, treated with at least one compound selected from the group consisting of the halides of acetic acid, hydrogen halides and iodine after spinning and drawing or shaping processes, and then treated with aliphatic amine compounds after washing.

By these treatments the excellent affinity of the fibres to anionic dyestuffs, such as acid dyestuffs, direct dyestuffs, chrome dyestuffs, metal complex dyestuffs, reactive dye-

stuffs, is obtained. The dyed materials have a very deep shade and good fastness. In the case of this invention, polypropylene fibres and the shaped articles showed little damage in tensile strength.

According to the present invention, polypropylene fibres and the shaped articles are dyed not only in a deep shade, but also in all tints of colour so that absolute black colour on the dyed materials can be obtained.

The bisamide compounds used in the present invention have good compatibility with polypropylene because of high hydrophobicity and nonpolarizability of the bisamide compounds, give no trouble in spinning and drawing or shaping processes and can maintain the obtained materials transparent.

The reasons why the polypropylene thus obtained in the present invention can be dyed very easily with anionic dyestuffs are not clear, but a high affinity for anionic dyestuffs would be attributed by the chemical change of the blended compounds and polypropylene, that is, by the easy penetration of halides of acetic acid, hydrogen halides or iodine into the fibres or the shaped articles where the molecular arrangement of the fibres or the shaped articles in amorphous region becomes considerably disordered by blending the said compounds, and by the amination of the fibres, in which the part subjected to the chemical change by halides of acetic acid, hydrogen halides or iodine are activated and easily aminated.

Bisamide compounds used in the present invention have a good heat stability, good compatibility with polypropylene in melting process and are represented by the following formula:



where  $R_1$  and  $R_3$  stand for alkyl group,  $R_2$  stands for alkylene group and  $X_1$  and  $X_2$  stand for  $-\text{NHCO}-$ ,  $-\text{CONH}-$ ,  $-\text{NHCOO}-$ , or  $-\text{COONH}-$  groups. Such bisamide compounds as methylene bisamides, ethylene bisamides, propylene bisamides, butylene bisamides, pentamethylene bisamides, hexamethylene bisamides, produced from capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachic acid, behenic acid, cerotic acid, montanic acid or mixture of them, are of value.

Before spinning or molding, these bisamide compounds are blended with polypropylene being in the form of powder or pellets in a quantity of from 1 to 25% based upon the weight of polypropylene.

The compounds used in the amine treatment are aliphatic amines, and especially ethylene diamine, hexamethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene-pentamine, and ethylene imine give good results.

The concentration of the acids and/or iodine, or the amines in these treatments are above 1% based upon the weight of the fibre, and the treatment is carried out for not less than a few seconds and at above room temperature. They depend upon the form of the fibres of the shaped articles. These treatments and rinsing can be carried out in a continuous or a discontinuous process.

The present invention is illustrated by the following examples in which percent is by weight.

**Example 1**

Crystalline polypropylene material having an average molecular weight of 77,000 was blended with 7% of methylene-bisstearamide of stearic acid and drawn to a length of 5 times the original one after melt-spun at 240° C. The resulted fibre was then immersed in a 50% aqueous monochloro acetic acid solution for 10 min. at 100° C., then completely rinsed with water, then also immersed in a 50% aqueous diethylene triamine solution at 80-90° C. for 60 min. and finally completely rinsed with water.

3

The tenacity and the elongation of thus treated fibre were 5.2 g./den. and 29.0%. The difference between the mechanical property of treated fibre and that of the untreated fibre are negligible.

Thus treated fibre was dyed in an acid dye bath containing 5% based upon the weight of fibre of an acid dyestuff, such as Supranol Blue BL (C.I. Acid Blue 59 C.I. 50315) or Supramine Red B (C.I. Acid Red 6 C.I. 14680) at 100° C. for 60 min. The dyed materials thus obtained were approximately same deep shade as nylon 6 fibre dyed with the same dyestuffs under the conditions as described above. However, fibre produced of polypropylene alone was hardly dyed, even if treated with a monochloro acetic acid solution and diethylene triamine solution under the same conditions as described above.

#### Example 2

The fibre produced of polypropylene blended with 3% of methylene bisstearamide and 3% of methylene bispalmitamide was immersed in a 50% aqueous solution of dichloro acetic acid at 100° C. for 20 min., thereafter completely rinsed with water, then also immersed in a 30% aqueous solution of ethylene diamine at 100° C. for 20 min. and finally completely rinsed with water.

Thus treated fibre was dyed in an acid dye bath containing 5% based upon the weight of fibre of an acid dyestuff, such as Solway Purple R (C.I. Acid Violet 43 C.I. 60730) at 100° C. for 60 min. Dyed materials have very deep shades.

#### Example 3

The fibre, produced of crystalline polypropylene blended with 3% of methylene bisamide was melt-spun and drawn as described in Example 1, was treated with a 40% aqueous solution of monochloro acetic acid at 100° C. for 15 min., thereafter completely rinsed with water, then also immersed in a 50% aqueous solution of hexamethylene diamine at 90° C. for 30 min. and finally completely rinsed with water.

Thus treated fibre was dyed in an acid dye bath containing 5% based upon the weight of fibre of a metal complex dyestuff, such as Cibalan Red 2GL (C.I. Acid Red 211) at 100° C. for 60 min. The dyed materials thus obtained have very deep shades.

#### Example 4

Crystalline polypropylene material having an average molecular weight of 66,000 was blended with 7% of ethylene bisstearamine, then melt-spun and drawn as described in Example 1. The resulting fibre was immersed in a 20% aqueous solution of hydrogen iodide at 100° C. for 3 min., completely rinsed with water, then also immersed in a 30% aqueous solution of triethylene tetramine at 100° C. for 20 min. and finally completely rinsed with water.

Thus treated fibre was dyed in an acid dye bath containing 5% based upon the weight of fibre of an acid dyestuff, such as Anthraquinone Green GNN (C.I. Acid 25 C.I. 61570) or a direct dyestuff, such as Japonol Brown M (C.I. Direct Brown 2 C.I. 22311) and Supraxel Violet 3RL (C.I. Direct Violet 51 C.I. 27905) at 100° C. for 60 min. Dyed materials have very deep shades. However, fibre produced of polypropylene alone was hardly dyed, even if treated with hydrogen iodide solution and amine under the same conditions as described above.

#### Example 5

Crystalline polypropylene material was blended with 3% of hexamethylene bisstearamide and then drawn to a length of 5 times the original one after melt-spun at 270° C. The resulted fibre was then immersed in 3% aqueous solution of iodine dissolved by potassium iodide at 100° C. for 10 min., completely rinsed with water, then also immersed in a 50% aqueous solution of tetra-

4

ethylene pentamine at 80–90° C. for 30 min. and finally completely rinsed with water.

Thus treated fibre was dyed in an acid dye bath containing 7% based upon the weight of fibre of direct dyestuff, such as Kayaku Direct Fast Black D (C.I. Direct Black 17 C.I. 27700) at 100° C. for 60 min. Dyed material of absolute black colour is obtained.

#### Example 6

Crystalline polypropylene material having an average molecular weight of 77,000 was blended with 2% of ethylenebisamide prepared from the mixture of 7 parts of stearic acid and 3 parts of palmitic acid. The resulted fibre was immersed in a 50% aqueous solution of monochloro acetic acid at 100° C. for 10 min., completely rinsed with water, then also immersed in a 2% aqueous solution of ethylene imine at 90° C. for 10 min. and finally completely rinsed with water. Thus treated fibre was dyed with the same dyestuff and the same condition as described in Example 1, and the dyed material have a very brilliant and deep shade.

#### Example 7

Crystalline polypropylene material was blended with 7% of methylene bisstearamide and then melt-spun and drawn as described in Example 1. Thus obtained fibre was immersed in a bath composed of the mixture of 20% of monochloro acetic acid and 2% of iodine dissolved in potassium bromide at 100° C. for 5 min., completely rinsed with water and then immersed in an 30% aqueous solution of diethylene triamine at 95° C. for 5 min. and completely rinsed with water.

The fibre thus treated was found to be dyed in a deep shade and in good fastness. The dyeing was carried out in an acid dye bath containing 5% based upon the weight of fibre of an acid dyestuff, such as Supranol Fast Cyanine 5R (C.I. Acid Blue 113 C.I. 26360), or a metal complex dyestuff, at 100° C. for 60 min.

However, fibre produced of polypropylene alone was hardly dyed and in a very poor fastness, even if treated under the same conditions as described above.

#### Example 8

The fibre produced of crystalline polypropylene blended with 7% of methylene bislauramide was melt-spun and drawn as described in Example 1, was immersed in a 60% aqueous solution of monochloro acetic acid at 100° C. for 5 min., thereafter completely rinsed with water, then also immersed in a 50% aqueous solution of diethylene triamine at 100° C. for 5 min. and finally completely rinsed with water.

Thus treated fibre was dyed with the same dyestuff and the same condition as described in Example 1, and the dyed material have a very deep shade.

#### Example 9

The fibre produced of crystalline polypropylene blended with 6% of methylene bisserotamide, was melt-spun and drawn as described in Example 1, was immersed in a 50% aqueous solution of monochloro acetic acid at 100° C. for 5 min., thereafter completely rinsed with water, then also immersed in a 50% aqueous solution of ethylenediamine at 100° C. for 30 min. and finally completely rinsed with water.

Thus treated fibre was dyed in an acid dye bath containing acid dyestuffs of 0.2% based upon the weight of fibre in the form of mixture at 100° C. for 60 min. Dyed material has very deep pastel colour.

#### Example 10

Crystalline polypropylene material was blended with 3% of ethylene bismyristamide and 4% of methylene bisarachiamide, then melt-spun and drawn. The resulting fibre was immersed in a 50% aqueous solution of hydrogen iodide at 100° C. for 10 min., completely rinsed with water, then also immersed in a 50% aqueous solu-

tion of hexamethylenediamine at 95° C. for 30 min. and finally completely rinsed with water.

Thus treated fibre was dyed in an acid dye bath containing 5% based upon the weight of fibre of a metal complex dyestuff, such as Vialon Fast Blue FFG, Vialon Fast Red G (C.I. Acid Red 226) and Vialon Fast Orange R (C.I. Acid Orange 89) at 100° C. for 60 min. Thus dyed materials are in a very deep shade, and these colour fastnesses, such as washing, drycleaning, rubbing, are excellent.

What we claim is:

1. A process for improving the dyeability of polypropylene which comprises the steps of blending polypropylene with from 1 to 25 percent by weight based on the weight of polypropylene of a bisamide having the formula



wherein  $R_1$  and  $R_3$  are lower alkyl,  $R_2$  is lower alkylene and  $X_1$  and  $X_2$  are selected from the group consisting of —NHCO— and —CONH—; treating said blended polypropylene with an acid selected from the group consisting of monochloroacetic acid; dichloroacetic acid and trichloroacetic acid and then with a low molecular weight alkylene polyamine.

2. The process of claim 1, wherein said amine is selected from the group consisting of ethylene diamine, hexamethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine and ethylene imine.

3. The process of claim 1, wherein the bisamide is se-

lected from the group consisting of methylene bistearamide, methylene bispalmitamide, methylene bisamide, ethylene bistearamide, hexamethylene bistearamide and methylene bislauramide.

#### References Cited

##### UNITED STATES PATENTS

2,238,949	4/1941	Schlack	8—100
2,276,951	5/1942	Fisher	204—163
2,805,960	9/1957	Wolinski	117—38
2,991,264	7/1961	Monroe	260—32.6
2,932,550	4/1960	Walmsley	8—21
3,098,697	7/1963	Cappuccio et al.	8—55
3,112,199	11/1963	Camerini et al.	96—87
3,137,989	6/1964	Fior et al.	
3,165,492	1/1965	Tholstrup et al.	260—32.6
3,195,975	7/1965	Cappuccio	8—115.5

##### FOREIGN PATENTS

628,687	7/1963	Belgium.
3,817,083	5/1963	Japan.
3,820,718	1963	Japan.

##### OTHER REFERENCES

Kaeseman, German Auslegeschrift 1,083, 651, June 15, 1960.

NORMAN G. TORCHIN, *Primary Examiner*.

DONALD LEVY, *Examiner*.