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# DYEABLE POLYPROPYLENE FIBERS CONTAINING ALUMINUM SALTS

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This invention relates to dyeable polypropylene fibers. More particularly this invention relates to fibers which are produced by blending polypropylene with a reaction product of an alcoholate of the metal elements of the Groups II and III of the periodic table with an aliphatic carboxylic acid and subjecting to spinning and which process superior affinity for dyestuffs capable to combine with the metal contained in such fibers by coordinate bond or salt forming bond.

Polypropylene fibers have inherently various superior properties but can be dyed only with much difficulty. For this reason, a great deal of efforts have been tended toward the improvement of their dyeability. For example a graft-copolymerization method of various monomeric vinyl compounds on polypropylene, a spinning method of the polypropylene blended with a high molecular weight substance having affinity for dyestuffs, and that blended with an inorganic or organic salt (oxide or hydroxide) of metal, followed by dyeing with dyestuffs capable of forming coordinate bond or salt-forming bond with the said metal are among such attempts.

Generally speaking, the dyeing method which consists of introducing an inorganic metal salt to fibers followed by dyeing with dyestuffs capable of forming bond with the metal has been well known as a mordant dyeing method. However, on account of inferior affinity or compatibility of polypropylene with such a metal salt, this method cannot be applied to polypropylene. In other words, polypropylene hardly adsorbs such metal salt from its aqueous solution. Accordingly this method affords only a light color.

Even when such a metal salt is blended to spin with polypropylene, it is impossible to obtain good fibers because of the lack of compatibility and the lack of spinnability. It is possible to obtain fairly good fibers having fairly good dyeability if a metal salt of higher aliphatic carboxylic acid is used to blend and spin with polypropylene to improve compatibility.

Having observed the fact that both physical and mechanical properties and dyeability of fibers have been improved by the improvement of compatibility, we have found after extensive studies superior dyeable polypropylene fibers yielded by blending from 0.1 to 10 percent by weight of at least one kind of compound represented by a general formula of

$$(R_1COO)_mAl(OR_2)_n \quad (I)$$

wherein $R_1$ is an alkyl radical having from 7 to 29 carbon atoms, $R_2$ is an alkyl radical having from 1 to 28 carbon atoms, $m$ and $n$ are integers of 1 or 2 and $m+n=3$.

In general in the case of higher aliphatic carboxylic acid salt the molar ratio of aliphatic carboxylic radical to metal element can be selected from the range of 1:1 to 3:1, depending upon the valency of metal element and condition of preparation. In this case, when the above-mentioned molar ratio is in the range of 1:1 to 2:1, the valencies of metal other than those united with carboxylic acid are united with hydroxy radicals. Such compounds as expressed by general formula of $RCOOM(OH)_{1-2}$ or $(RCOO)_2M(OH)$, are not satisfactorily compatibile with



polypropylene. When the cross sections of dyed fibers containing such a compound are observed under a microscope, dyed sites are observed as colored spots. By measuring the dye-adsorption, it will become clear that the efficiency of metal atom as dyeing sites is low. Compounds in which all the valencies are united with carboxyl radicals show superior compatibility, and no colored spots are observed in the cross-section of dyed fiber, affording uniform dyeing. However since the relative amount of metal vs. molecular weight is little, it is necessary to increase the amount to be blended, and also in this case, the efficiency of dyeing sites is not sufficiently high.

On the other hand, those compounds represented by the above-mentioned general formula i.e. above-mentioned compounds in which hydroxy radicals are replaced by alkoxy radicals show exceedingly good compatibility. No colored spots are observed in the cross sections of dyed fiber. By measuring the dye adsorption, it becomes clear that the efficiency of dyeing sites is very high. Moreover since even the compound in which $R_2$ of the above-mentioned general formula is an alkyl radical having only 1 to 4 carbon atoms affords sufficient compatibility, the relative amount of the metal to molecular weight is not lowered. Accordingly it is not necessary to blend large amounts of this compound to obtain higher dyeability.

When compounds containing metal bleeds out into dye bath during the operation of dyeing, there will occur the combination of dyestuff with metal atom. Since this combined product does not show any affinity with polypropylene fiber, this means the waste of so much amount of dyestuff. Besides this, the bleeding of additives into dye bath brings about various troubles. Compounds used in the present invention does not show such bleeding. The superior compatibility of the compounds of the present invention can be seen from this fact as well.

As for metals of the general Formula I, metal elements of II and III groups of the periodical table are useful, but particularly aluminum affords the best effect among them.

$R_1$ is an alkyl radical. The number of carbon atoms of $R_1$ varies according to the value of $m$ and $n$. It is generally in the range of from 7 to 29, preferably from 11 to 17. In other words, compounds having a structure of derivative of aliphatic carboxylic acid salt having from 8 to 30, preferably from 12 to 18 carbon atoms are preferable. When $m$ is 2, the number of carbon atoms of $R_1$ can be relatively small, but when m is 1, and the number of carbon of $R_1$ is small, sufficient compatibility cannot be obtained unless the number of $R_2$ is relatively large. In such a case the efficiency of dyeing sites is low. It is rather difficult to obtain deep color, compared with the case when the number of carbon atoms of $R_1$ is large and that of $R_2$ is small.

$R_2$ is an alkyl radical. It is possible to increase the compatibility sufficiently high with the number of carbon atoms of from 1 to 18, preferably from 2 to 12. It is not preferable to improve compatibility excessively by increasing the number of carbon atoms of $R_2$ since the utilization efficiency of dyeing sites is lowered as mentioned above. When the case of $m$ being 1 and $n$ being 2 is compared with that of $m$ being 2 and $n$ being 1, the latter case shows excellent dyeability.

The amount of blending of compounds expressed by the general formula of (1) vs. polypropylene varies according to values of $R_1$, $R_2$, $m$, and $n$. It is preferable to select it in the range of from 0.1 to 10 percent by weight most preferably from 1 to 5 percent, considering the mechanical properties and dyeability of fibers. When the blending amount is increased, the dyeability is improved, affording deep color easier, but the mechanical properties of fibers are lowered. When the blending amount is lowered, the mechanical properties are increased but sufficient dyeability cannot be obtained.

Representative compound expressed by the above-mentioned general formula useful in the present invention include stearoyloxy-diisopropoxy-aluminum, lauroyloxy - diisopropoxy - aluminum, stearoyloxy - dimethoxy-aluminum, stearoyloxy-diethoxy aluminum, lauroyloxy-diethoxy-aluminum, lauroyloxy dilauroxy-aluminum, distearoyloxy - monomethoxy - aluminum, distearoyloxy-monoethoxy - aluminum, distearoyloxy - monobutoxy-aluminum, dilauroyloxy-monoisopropoxy-aluminum, and dioctoyloxy-monoisopropoxy-aluminum.

These compounds can be produced readily by heating a metal alkoxide prepared by ordinary method with a calculated amount of aliphatic carboxylic acid in an organic medium.

In practice of the present invention, it is possible to add various stabilizers and other additives commonly used for polyolefin.

As dyestuffs useful for dyeing fibers of the present invention, those which can combine with metals (especially aluminum) of the compound are useful. In other words, beside general mordant dyes, "Mayfon" dyestuffs "Koprolene" dyestuff "Verona" dyestuffs and "Olefine" dyestuffs which have been developed for metal-containing polypropylene fibers, are suitable.

As for dyeing methods, ordinary methods can be used, and by use of, if necessary, non-ionic surfacants or anionic surfacants, as a dye assistant, by maintaining pH at from 2 to 8 (weak acids are used for controlling), by boiling and dyeing at atmospheric pressure it is possible to obtain beautiful and fast dyed products.

In producing dyeable polypropylene fibers of the present invention, any of common melt-spinning, wet-spinning and dry-spinning processes can be applied.

The following examples are given to illustrate the present invention but the invention is not restricted to these examples.



Stearoyl-oxy-diisopropoxy-aluminum (A) and crystalline polypropylene powder having an intrinsic viscosity of 1.4 measured in tetralin at 135° C. were blended in proportions shown in Table 1, made into pellets at a temperature of 220° C., subjected to common melt-spinning method, and stretched at a temperature of 130° C. to produce fibers.

Resulting fibers were subjected to scouring, dyeing and soaping at following conditions thereby to obtain red-colored fibers. Results of these treatment are shown in Table 1.

*Scouring*

| | |
|---|---|
| "Scourol No. 400," g./l | 0.5 |
| Sodium pyrophosphate, g./l | 0.1 |
| Liquor ratio | 1:50 |
| Temperature, ° C | 70 |
| Time, min | 30 |

After treated, fibers were washed with water.

*Dyeing*

| | |
|---|---|
| "Mitsui Alizarine B," percent, O.W.F | 3 |
| A surfactant, "olomin" whose principal composition is sodium alkyl-aryl sulfonate, g./l | 1 |
| Formic acid, percent, O.W.F | 2 |
| Liquor ratio | 1:50 |

Temperature was elevated from 50° C. to 90° C. in 30 minutes and dyeing was carried out at this temperature for 90 minutes, followed by washing with water and by soaping.

*Soaping*

| | |
|---|---|
| "Scourol No. 400," g./l | 0.5 |
| Sodium carbonate, g./l | 0.1 |
| Liquor ratio | 1:50 |
| Temperature, ° C. | 90 |
| Time, min | 20 |

After treated, fibers were washed with water.

TABLE 1

| No. | Polypropylene (weight percent) | Substance A (weight percent) | Dry tenacity (g./d.) | Dry elongation (percent) | Percent dye adsorbed | Fastness | |
|---|---|---|---|---|---|---|---|
| | | | | | | Sunlight | Wash |
| 1 | 100 | 0 | 6.5 | 28.5 | 0 | | |
| 2 | 99 | 1 | 6.4 | 27.0 | 65 | 5 | 5 |
| 3 | 98 | 2 | 6.5 | 25.8 | 71 | 6 | 5 |
| 4 | 97 | 3 | 6.2 | 26.4 | 73 | 6 | 5 |
| 5 | 96 | 4 | 6.4 | 28.0 | 75 | 6 | 5 |

*Example 1*

27 parts by weight of aluminum powder, 300 parts by weight of anhydrous isopropyl alcohol, and 0.5 part by weight of mercuric chloride were introduced and heated in a 2 l. flask. When boiling started, 2 parts by weight of carbon tetrachloride were added thereto. Reaction proceeded violently while forming. Heating was continued for about 5 hours and further the reaction mixture was maintained at a temperature of 70° C. overnight. Subsequently insoluble substances were settled, supernatant liquid was subjected to distillation under reduced pressure of 1 mm. Hg and distillate at a temperature ranging from 125° C. to 132° C. was collected by which about 190 g. of aluminum triisopropoxide were obtained.

20.4 parts by weight of aluminum triisopropoxide and 28.4 parts by weight of stearic acid were heated and reacted in 200 parts by weight of benzene at a temperature of boiling point of benzene for 2 hours. When reacted mixture was dropped in ethanol, 46 parts by weight of stearoyl-oxy-diisopropoxy-aluminum

$$C_{17}H_{35}COO \cdot Al(OC_3H_7)_2$$

in the form of readily crushed amorphous blocks were obtained. This substance did not show a sharp melting point and its softening point was about 200° C.

In this table and hereinafter the sunlight fastness was determined by the carbon arc method of Japanese Industrial Standards JIS–L1044 (1959) and the wash fastness was expressed by beaker method BC–2 of JIS–L1045 (1959).

*Example 2*

The same fibers used in Example 1 were dyed in a dye bath which contained 5 percent O.W.F. of "mayfon yellow 395" paste and controlled to the pH of from 3.5 to 4.0 (by adding formic acid). The other dyeing condition were same as in Example 1. Resulting dye adsorption are shown in the following Table 2.

TABLE 2

| Fibers: | Percent-dye adsorbed |
|---|---|
| No. 1 | 0 |
| No. 2 | 85 |
| No. 3 | 89 |
| No. 4 | 92 |
| No. 4 | 95 |

The light fastnesses were all grade 6 and the wash fastness were all grade 5.

*Example 3*

50 parts by weight of aluminum powder were dispersed in 325 parts by weight of xylene, and the resulting suspension was heated to reflux. 220 parts by weight of anhydrous ethanol added with 0.25 part by weight of mercuric chloride and a small amount of iodide, were dropped in the suspension.

After finishing the addition of total ethanol, heating was continued. After termination of hydrogen gas evolution was subsided, the suspension was filtered and while flushing nitrogen, xylene was driven off at a reduced pressure, whereby 200 g. of aluminum triethylate were obtained. 162 parts by weight of aluminum triethylate and 284 parts by weight of stearic acid were dissolved in benzene and brought to the reaction at the boiling temperature of benzene for about 2 hours. Then ethanol was added to precipitate the product, whereby, 435 parts by weight of dried monostearolyoxy diethoxy aluminum (substance B) were obtained.

The same crystalline polypropylene as in Example 1 was blended with this substance in proportions as shown in Table 3, made into pellets at a temperature of 220° C., subjected to a ordinary melt spinning process at a temperature of 250° C. and stretched 5 times the original length at a temperature of 130° C. to produce fibers.

These fibers were subjected to the same scouring as in Example 1. After washing with water, the fibers were dyed in a dye bath containing 3 percent O.W.F. of "Sunchromine Pure Blue B ex" and 5 percent O.W.F. of 48 percent acetic acid, at a liquor ratio of 1:50, at a temperature of 98° C. for 90 minutes. In the course of dyeing, 4 percent O.W.F. of 85 percent acetic acid were added. Subsequently, dyed substances were taken out and subjected to soaping as in Example 1.

All of the resulting dyed fibers had bright blue color. There were no discoloration observed after irradiation with a fadeometer for 48 hours. The wash fastness was excellent and of grade 5. Results of fiber properties and dye adsorption are shown in Table 3.

TABLE 3

| No. | Composition polypropylene (weight percent) | Substance B (weight percent) | Dry tenacity (g./d.) | Dry elongation (percent) | Percent dye adsorbed |
|---|---|---|---|---|---|
| 1 | 99 | 1 | 6.7 | 28.0 | 56 |
| 2 | 98 | 2 | 6.5 | 29.0 | 60 |
| 3 | 95 | 5 | 6.6 | 29.5 | 65 |
| 4 | 90 | 10 | 5.8 | 32.4 | 85 |

*Example 4*

The same fibers as in Example 3 were dyed in a dye bath containing 5 percent O.W.F. of "Olefin Blue 15702" made acidic by acetic acid (pH 4–5) according to the method of Example 1.

The hue of resulting products was bright violet and the dye adsorption and the fastness were excellent as shown in Table 4.

TABLE 4

| No. | Percent dye adsorbed | Sunlight fastness grade | Wash fastness grade |
|---|---|---|---|
| 1 | 75 | 5 | 5 |
| 2 | 87 | 6 | 5 |
| 3 | 91 | >6 | 4–5 |
| 4 | 89 | >6 | 4–5 |

*Example 5*

By the same procedure as in Example 1 except that stearic acid alone was used twice as much, following compounds were obtained. $(C_{17}H_{35}COO)_2AlOC_3H_7$ (substance D).

Crystalline polypropylene having an intrinsic viscosity of 1.6 were blended with the substance D in proportions shown in Table 5 and subjected to a customary melt spinning method to produce fibers. These fibers were dyed by "Mitsui Alizarine Blue S" under the same condition as in Example 1, whereby the fibers were dyed to bluish violet. Fiber properties and dyeability are shown in Table 5.

TABLE 5

| No. | Polypropylene (weight percent) | Substance D (weight percent) | Dry tenacity (g./d.) | Dry elongation (percent) | Percent dye adsorbed | Fastness | |
|---|---|---|---|---|---|---|---|
| | | | | | | Sunlight (Grade) | Wash (Grade) |
| 1 | 99.5 | 0.5 | 6.5 | 27.5 | 75 | 6 | 5 |
| 2 | 99 | 1 | 6.4 | 28.0 | 88 | 6 | 5 |
| 3 | 98 | 2 | 6.3 | 29.5 | 95 | >6 | 5 |
| 4 | 96 | 4 | 6.2 | 31.0 | 97 | >6 | 5 |

*Example 6*

Substances indicated in Table 6 were blended with crystalline polypropylene in an amount of 2 percent by weight. Fibers were produced according to the same method as in Example 1 from this blend. Resulting fibers were dyed as in Example 2. The results are shown in Table 6.

TABLE 6

| No. | Additives | Dry tenacity (g./d.) | Dry elongation | Percent dye adsorbed |
|---|---|---|---|---|
| 1 | $(C_{17}H_{35}COO)_2AlOC_2H_5$ | 6.5 | 29.5 | 95 |
| 2 | $(C_{17}H_{35}COO)_2AlOC_4H_9$ | 6.5 | 29.8 | 94 |
| 3 | $(C_{17}H_{35}COO)_1Al(OC_2H_5)_2$ | 6.2 | 25.8 | 90 |
| 4 | $(C_{17}H_{35}COO)_2AlOH$ | 6.0 | 30.1 | 77 |
| 5 | $(C_{17}H_{35}COO)_1Al(OH)_2$ | 5.87 | 32.0 | 85 |

No. 4 and No. 5 are illustrated as controls.

The sunlight fastnesses of resulting products were all higher than 5 grade and the wash fastness were excellent and found to be 5 grade.

When the cross-section of these dyed products were observed under a optical microscope, No. 1 and No. 2 were found to be dyed uniformly. No. 3 was also uniform but some deeply dyed spots were found scattered. No. 4 showed the same dispersity. No. 5 had many such spots and dyestuff was found almost on the spotted dyed places. It is apparent that the compatibility of the present additives is excellent.

*Example 7*

The same fibers as in Example 5 were dyed by 5 percent O.W.F. of "Koprolene Garnet R" according to the method of Example 4.

The hue of resultant dyed products was bright orange, cross sections of dyed fibers were found to be uniformly dyed, and the dye adsorption and the fastness were excellent as shown in Table 7.

TABLE 7

| No. | Percent dye adsorbed | Sunlight fastness | Wash fastness (grade) |
|---|---|---|---|
| 1 | 77 | 5-6 | 5 |
| 2 | 86 | 5-6 | 5 |
| 3 | 92 | 6 | 5 |
| 4 | 93 | 6 | 4-5 |

What we claim is:

1. Dyeable polypropylene fibers comprising polypropylene and from 0.1 to 10 percent by weight of at least one of the compound represented by a general formula of $(R_1COO)_mAl(OR_2)_n$ wherein $R_1$ is an alkyl radical having from 7 to 29 carbon atoms, $R_2$ is an alkyl radical having from 1 to 18 carbon atoms, $m$ and $n$ are integers selected from the group consisting of 1 and 2 with a condition of $m+n=3$.

2. Dyeable polypropylene fibers comprising polypropylene and from 0.1 to 10 percent by weight of at least one of the compound represented by a general formula of $(R_1COO)_mAl(OR_2)_n$ wherein $R_1$ is an alkyl radical having from 7 to 17 carbon atoms, $R_2$ is an alkyl radical having from 2 to 12 carbon atoms, $m$ and $n$ are integers selected from the group consisting of 1 and 2 with a condition of $m+n=3$.

3. Dyeable polypropylene fibers comprising polypropylene and from 1 to 5 percent by weight of at least one of the compounds represented by a general formula of claim 1.

4. Dyeable polypropylene fibers comprising polypropylene and from 0.1 to 10 percent by weight of at least one of the compounds represented by a general formula of claim 1, except the values of $m$ and $n$ being 2 and 1 respectively.

5. Dyeable polypropylene fibers comprising polypropylene and from 1 to 5 percent by weight of at least one of the compounds represented by a general formula of claim 1, except the values of $m$ and $n$ being 2 and 1 respectively.



6. Dyeable polypropylene fibers comprising polypropylene and from 1 to 5 percent by weight of at least one of the compounds represented by a general formula of claim 2.

7. Dyeable polypropylene composition comprising polypropylene and from 0.1 to 10 percent by weight of at least one of the compounds represented by a general formula of claim 2 except the values of $m$ and $n$ being 2 and 1 respectively.

8. Dyeable polypropylene composition comprising polypropylene and from 1 to 5 percent by weight of at least one of the compounds represented by a general formula of claim 2 except the values of $m$ and $n$ being 2 and 1 respectively.

9. Dyeable polypropylene fibers comprising polypropylene and from 1 to 10 percent by weight at least one of the compounds selected from the group consisting of stearoyl-oxydiisopropoxy-aluminum, lauroyloxy-diisopropoxy-aluminum, stearoyloxy-dimethoxy-aluminum, stearoyloxy-diethoxy-aluminum, lauroyloxy - diethoxy - aluminum, lauroyloxy - dilauroxy - aluminum, distearoyloxy-monomethoxy-aluminum, distearoyloxy-monoethoxy-aluminum, distearyloxy - monobutoxy - aluminum, dilauroyloxy-monoisopropoxy-aluminum and dioctoyloxy-monoisopropoxy-aluminum.


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