

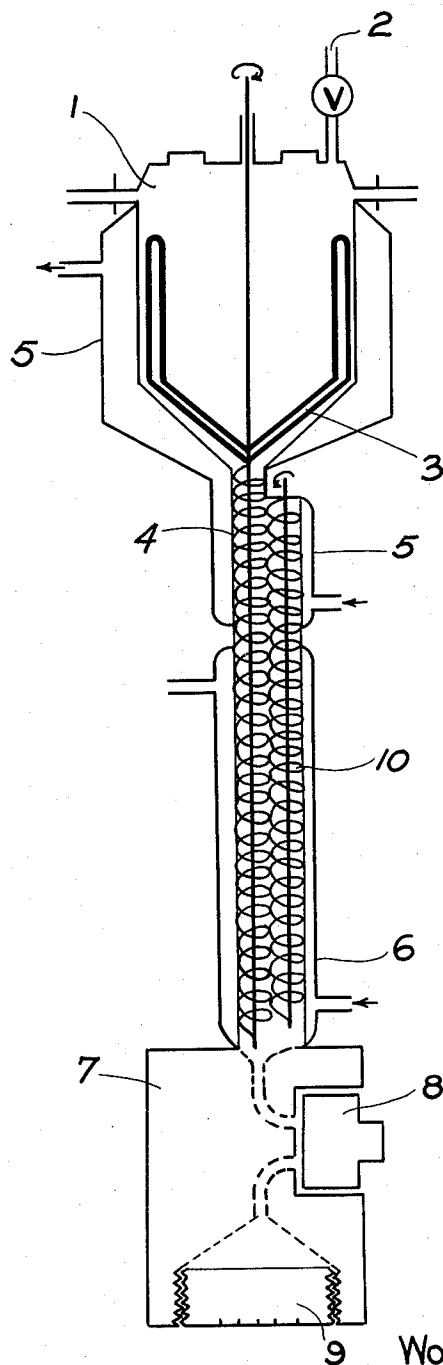
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METHOD OF PREPARING STABLE POLYOLEFIN DISPERSION

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METHOD OF PREPARING STABLE POLYOLEFIN DISPERSION

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The invention relates to the production of filamentary aliphatic polyolefines, and in particular, to an improved method of preparing a high molecular weight polyolefine spinning solution to be employed in the extrusion or spinning of fine filaments, fibers or the like.

The production of high molecular weight polyolefine filaments is more fully described in my copending application, Serial No. 664,289, filed June 7, 1957, the disclosure of which is incorporated herein by reference as fully as if it had been set forth in its entirety. In this copending application there is described a process whereby a high molecular weight polyolefine prepared by the so-called low pressure polymerization of an olefine having from 2 to 5 carbon atoms, i.e., ethylene, propylene, butylene and pentene, is dissolved in a hot liquid petroleum oil consisting essentially of paraffin and/or naphthene hydrocarbons so as to obtain an at most 18% solution of the polyolefine, and the solution is then extruded or spun into fine filaments. The filaments obtained by spinning these solutions, especially solutions of polyethylene having a molecular weight of at least 70,000, exhibit an excellent tensile strength and are generally superior by comparison to filaments of low molecular weight polyolefines which have been prepared by the so-called high pressure process and spun from the melt or from a solution.

The expression "high molecular weight polyolefine" is employed herein to define a polyolefine having a molecular weight of about 70,000 or higher and which is prepared by the low pressure process. Polyethylene prepared by the low pressure process is particularly characterized by a virtually unbranched carbon chain.

The expression "low molecular weight polyolefine" is employed herein to define a polyolefine which has a molecular weight of about 5,000 to 60,000 and which is prepared by a high pressure process.

In the copending application referred to above, the high molecular weight polyolefine is spun from the oil solvent spinning solution at a constant elevated temperature, e.g., 150–250° C., and subsequently precipitated and stretched several times its original length. On a laboratory basis, no particular difficulty is encountered in preparing the spinning solution since it is possible to work with relatively small quantities. However, when a continuous spinning process is to be executed on a relatively large scale, it is necessary that a substantial quantity of a polyolefine powder be uniformly dispersed in the petroleum oil solvent and stored in a tank or other suitable vessel from which the small portion required for spinning is immediately available after a simple heating. It is advisable to store the spinning solution at about room temperature or slightly below, preferably at about 10° C. to 25° C., even though the polyolefine does not dissolve at this low temperature and must be uniformly dispersed as a finely divided powder in the hydrocarbon oil.

It was found, however, that when spinning over a relatively long period of time, e.g., up to 24 hours and longer,

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that the supply of the polyolefine in dispersed form is unstable and produces a rapid deposition of the polyolefine powder even during constant stirring. This phenomenon of deposition is extremely disadvantageous because it is impossible under these conditions to maintain a constant concentration of the polyolefine in the subsequent heated spinning solution. Even the paraffin oils which are known to have the best solvent effect upon polyethylene, for example, do not alleviate this condition which occurs in the dispersion form of the spinning composition.

In accordance with the invention, it has now been discovered that this problem of deposition from the polyolefine-solvent dispersion can be avoided for all practical purposes by following the procedure hereinafter set forth. This novel procedure is described with reference to polyethylene but is equally applicable to polypropylene, polybutylene, and polypentene so that the description and examples are intended to be illustrative only and not exclusive.

The improved method of preparing a stable dispersion which can be heated to form a spinning solution requires that first a low concentration solution be obtained by dissolving in the petroleum oil solvent a small quantity of about 0.01% by weight, and preferably about 0.5% by weight, up to not more than 2% by weight of a finely powdered polyethylene. A true solution can be obtained at elevated temperatures above the melting point of the polyethylene, preferably at temperatures of about 140° C. or more. This at most 2% solution is then cooled to about room temperature, e.g., to a temperature of between 0° C. and 40° C., preferably between about 5° C. and 25° C. Either a low or high molecular weight polyethylene may be employed to prepare this initial solution. If only a high molecular weight polyethylene is employed, this solution may be used directly for spinning filaments after again heating. However, this low concentration of polyethylene does not provide the most desired properties in a polyethylene filament.

Surprisingly, it was found that additional amounts of a finely powdered polyethylene can be added to the initial solution and uniformly dispersed therein by sufficient stirring or mixing without showing any pronounced tendency toward a deposition of polymer particles. Accordingly, a high molecular weight polyethylene powder is then added to the at most 2% solution of either a low or high molecular weight polyethylene so as to obtain the preferred properties of a polyethylene having a molecular weight of at least 70,000. It is essential, however, that the total content of polyethylene in the oil solvent be not more than 18% by weight, preferably between about 12 and 16% by weight. Where a low molecular weight polyethylene is employed in the 0.01–2% dispersion, the high molecular weight polyethylene should provide an at least predominant proportion of the total polyethylene content. It is particularly advantageous to have at least five times as much of the high molecular weight polyethylene in this instance. Thus, in all cases, it is preferable to add about 10 to 16% by weight of the finely divided polyethylene powder to an initial 0.5–2% solution.

The polyolefine-solvent dispersions containing at most 18% of the polyolefine which are prepared by the method of the invention can be produced in relatively large quantities for storage and thereby provide a composition which can be readily heated to obtain a spinning solution with an accurately adjusted and constant concentration. Generally speaking, the dispersed phase polyolefine can be stored for periods of 24 hours and longer without any substantial deposition, such periods of time being normal under the ordinary conditions which might be expected in a commercial application of the process.

Suitable petroleum oil solvents within the scope of the invention are those which are obtained as the intermediate to heavy distillates in the fractionation of petroleum and which have intermediate boiling points, e.g., between 150° C. and 380° C. or higher, preferably above 150° C. up to about 300° C. These solvents consist essentially of paraffin and naphthene hydrocarbons as mixtures which are commonly known under such commercial or familiar names as mineral oil, gas oil, paraffin oil, spindle oil, white oil, and the like. The terms "paraffin" and "naphthene" refer to saturated aliphatic and cycloaliphatic hydrocarbons.

Of course, the solvent employed herein must be in the liquid phase during storage of the polyolefine dispersion as well as at the spinning temperatures. The saturated hydrocarbon oils should also have a somewhat viscous consistency and are preferably as colorless as possible. The selection of suitable solvents having these various properties can be easily accomplished by one who is familiar with the usual requirements of a spinning process.

While either a low or high molecular weight polyolefine can be used in the initial dispersion of not more than 2% concentration, the polymers having molecular weights of over 70,000 are preferred. Likewise, even with the low molecular weight polymers, those having a molecular weight of, for example 25,000 to 50,000 are preferred over those of 5,000 to 25,000.

The following examples further illustrate the present invention with reference to the accompanying drawing which indicates suitable apparatus especially adapted for preparing the spinning solution and the subsequently spinning of filaments therefrom. The abbreviation "Rkm" which appears in the following examples stands for Reißkilometer, one unit Rkm being equal to 9 grams per denier.

Example I

A polyethylene of a molecular weight 125,000 is dissolved at 180° C. in a gas oil with a boiling point of 225° to 230° C. to obtain a 0.5% solution. This polyethylene solution, after cooling to about room temperature, is employed for the preparation of a more concentrated dispersion. For this, 14% by weight of polyethylene powder of a molecular weight of 125,000 is stirred into the cooled solution. The dispersion prepared in this manner has a tendency to deposit polyethylene particles only after about 24 hours of standing.

The dispersion is converted to a heated spinning solution and spun in the apparatus shown in the accompanying drawing. The dispersion is first stored in the dispersion tank 1, cooled to about 20° C., and placed under a pressure of about 3 atmospheres of a substantially inert gas (e.g., nitrogen or compressed air). The gas inlet is indicated at 2. The dispersion tank contains a stirrer or other suitable mixing device 3, which is securely connected with the dissolving and mixing worm 4 and turns at the same rate as the worm. Parallel to the worm 4 there is a second worm 10, so that by an intensive kneading or mixing with the double worm, an especially uniform and rapid dissolving effect can be achieved. The upper part of the double worm and the dispersion tank are surrounded by a cooling mantle or jacket 5. The lower part of the double worm is surrounded by a heating jacket 6, which is heated to about 180–220° C., preferably about 200° C. As soon as the polyethylene-gas oil dispersion is conveyed from the dispersion tank downward into and through the hot region of the double worm, the dispersed polyethylene powder is converted into a clear viscous solution. This solution first enters through the pumping block 7 into the spinning pump 8 and is then conveyed to the spinning head 9. The pumping and spinning head are likewise heated in a conventional manner, preferably to about 200° C.

The spinning solution produced in the hot portion of the double worm (14.5% solution) is spun through a

30-hole spinning head 9 at a rate of 14.4 cm.³/min. with the pressure exerted by the spinning pump 8. The nozzle openings or spinning orifices have a diameter of 200μ each. The threads or filaments of the heated solution emerge from the spinning head, and after traversing a 10 cm. long air space, are then conducted through a 20° C. warm precipitation bath of propanol. The filaments then pass into a washing bath of petroleum ether, the bath having a length of 4 meters. Thereafter, in a 4 meter hot water bath maintained at 95° C., the filaments are stretched to double their original length. The filaments are then again washed in a petroleum ether washing tube. Finally, in a hot glycerine bath at about 124° C., the filaments are again stretched to 4 times their length (a total stretching, therefore, of eight times the original spun length).

The resulting filaments have a strength of 100 Rkm at 6% elongation and an individual titer of approximately 1.4 denier.

Example II

Polyethylene of a molecular weight of 50,000 (produced by the high-pressure process) is dissolved at 150° C. in a gas oil having a boiling point of 225–230° C. to produce a 1% solution of polyethylene. The dissolving requires about 5 minutes. After cooling the 1% solution, approximately 13% by weight of a finely powdered polyethylene of a molecular weight of 150,000 is uniformly dispersed in the initial solution by stirring. The resulting 14% dispersion of polyethylene shows no appreciable particle deposition, even after standing for 24 hours.

The further treatment of this 14% dispersion including storage followed by heating to obtain a hot spinning solution and the subsequent spinning of filaments is accomplished with the same apparatus and in the same manner as that described in Example I. The filaments are conducted through a 4 meter washing bath containing petroleum ether and pass immediately into a glycerine bath heated to 124° C. where they are stretched to 8 times their original length. The resulting filaments have a strength of 84 Rkm at 14% elongation and an individual titer of approximately 2.3 denier.

The invention is hereby claimed as follows:

1. An improved method of preparing a stable dispersion of a high molecular weight polyolefine capable of being heated to form a spinning solution which comprises: dissolving at a temperature above about 140° C. in a hot liquid petroleum oil selected from the group consisting of paraffin and naphthene hydrocarbons from 0.01 to not more than 2 percent by weight of a low to high molecular weight polyolefine of the group consisting of poly-ethylene, -propylene, -butylene and -pentene; cooling the resulting solution to from about 0° C. to 40° C.; and uniformly dispersing in said cooled solution a finely powdered high molecular weight polyolefine of said group, the total content of polyolefine in said oil being not more than 18 percent by weight of which at least a predominant proportion has a high molecular weight of at least about 70,000.

2. An improved method as defined in claim 1 wherein the polyolefine is polyethylene.

3. An improved method as defined in claim 1 wherein the polyolefine is polypropylene.

4. An improved method as defined in claim 1 wherein the polyolefine is polybutylene.

5. An improved method as defined in claim 1 wherein the polyolefine is polypentene.

6. An improved method of preparing a stable dispersion of a high molecular weight polyethylene capable of being heated to form a spinning solution which comprises: dissolving at a temperature above about 140° C. in a hot liquid petroleum oil selected from the group consisting of paraffin and naphthene hydrocarbons from about 0.5 to not more than 2 percent by weight of a low to

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high molecular weight polyethylene; cooling the resulting solution to from about 10° C. to 25° C.; and uniformly dispersing in said cooled solution about 10 to 16 percent by weight of a finely powdered polyethylene having a high molecular weight of at least 70,000, the total content of polyethylene in said oil being not more than 18 percent by weight.

7. An improved method as defined in claim 6 wherein

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the total content of polyethylene has a high molecular weight of at least 70,000.

References Cited in the file of this patent

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