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PROCESS OF EXTRUDING FIBERS FROM A MOLTEN POLYAMIDE CONTAINING A PHOSPHOROUS COMPOUND

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9 Claims. (Cl. 260—30.6)

This invention relates to a process for the melt spinning of a filamentary structure from a synthetic nitrogen-containing polymer. More particularly, it is concerned with an improved process for the formation of a filament, yarn, ribbon or the like by melt spinning a synthetic linear fiber-forming polyamide.

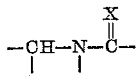
It has been suggested that the utility of synthetic fibers could be increased and their properties, in particular their dyeability, could be improved if the concentration of amine end groups in the polyamides could be increased. Polymers with increased amine end group concentration have been prepared but serious problems were encountered in melt spinning due to the frequent occurrence of "drips" of the molten polymer as it emerges from the spinneret. The increased concentration of amine end groups considerably increases the frequency of drips making frequent interruption of the spinning process necessary for wiping off the spinneret. These "drips" are very frequent when the polymer contains a hydrogen atom on the carbon atom alpha to the nitrogen of the amide group in the main polymer chain. The frequent interruptions are inhibitive, if not prohibitive, to commercial operation of such processes.

It is an object of the present invention, therefore, to provide a synthetic yarn with improved dyeability and an improved process for its preparation.

Another object is to reduce the number of drips when melt spinning a nitrogenous polymer containing —CH— groups adjacent to the nitrogen atom of the amide group in the main polymer chain.

A still further object is to provide an improved melt-spinning process for a synthetic linear fiber-forming polyamide, preferably polycarbonamides, having an increased concentration of amine end groups so that "drips" are eliminated or substantially reduced.

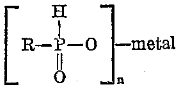
These objects are accomplished by the present invention which provides an improvement in the process for the formation of a filamentary structure of a synthetic linear fiber-forming polymer having a structural unit of the formula



$$-\underset{|}{\mathrm{CH}}-\underset{|}{\mathrm{N}}-\overset{\overset{\displaystyle X}{\|}}{\mathrm{C}}-$$

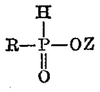
wherein X is selected from the group consisting of oxygen and sulfur in at least 50% of the recurring units of the main polymer chain and having from about 55 to 160 gram equivalents of amine end groups per 10^6 grams of polymer, by extruding the molten polymer through an orifice into a quenching medium, the improvement comprising dissolving in the extrudate prior to extrusion at least 0.05% by weight, based on the weight of the

polymer, of a phosphorus compound selected from the group consisting of a compound of the formula



$$\left[\mathrm{R}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle O}{\|}}{\mathrm{P}}}-\mathrm{O}\right]_n\!-\mathrm{metal}$$

and a compound of the formula



$$\mathrm{R}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle O}{\|}}{\mathrm{P}}}-\mathrm{OZ}$$

wherein

R is selected from the group consisting of alkyl, cycloalkyl, aryl and arylalkyl,

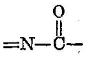
n is a whole number corresponding to the valence of the metal,

Z is selected from the group consisting of hydrogen, alkyl, aryl, arylalkyl, and alkyl substituted ammonium cation, and

R and Z being alkylene when joined to form a ring structure.

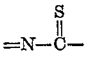
The term "filamentary structure" is used to signify an article which has two dimensions which are small as compared to its third dimension. The term includes filaments, fibers, yarns, ribbons, thread and the like.

By "a synthetic linear fiber-forming polymer . . . the main polymer chain" is meant a wholly synthetic, or man-made, polymer which contains a preponderance of recurring units containing a hydrogen atom on the carbon alpha to the nitrogen atom of the amide (including thioamide) unit of the chain. Such polymers include the polycarbonamides, polythioamides, polyureas, polythioureas, polyurethanes and the like and all such polymers may be broadly defined as the polyamides since they contain either the carbonamide unit



$$=\mathrm{N}-\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}-$$

or the thioamide unit



$$=\mathrm{N}-\overset{\overset{\displaystyle S}{\|}}{\mathrm{C}}-$$

as the linking units in the main polymer chain. In a preferred embodiment of the present invention, the polymer is a polycarbonamide and contains from 90 to 100% of such groups containing the hydrogen atom on the alpha carbon atom.

The terminology "having from about 55 to 160 gram equivalents of amine end groups per 10^6 grams of polymer" signifies a polymer which contains an unusually high number of amine end groups. The method of measuring the amine end groups may be found in G. B. Taylor and J. E. Waltz "Anal. Chem.," vol. 19, page 448, (1947).

The expression "by extruding the molten polymer through an orifice into a quenching medium" is employed to mean the conventional melt-spinning process whereby the polymer is melted and forced through a hole or slot into a medium such as a liquid or gas, generally an inert gas, to cool and solidify the polymer into a long, substantially continuous structure.

The terminology "dissolving in the extrudate prior to extrusion" is used to indicate that at the time of extrusion the polymer contains in a dissolved form one or more of the desired compounds. The compounds may, of course, be added to the polymer ingredients prior to polymerization or they may be added to the polymer itself prior to extrusion. In addition, the compounds may be formed in situ. In any event, the phosphorus compound is present in the polymer in the dissolved state during extrusion in quantities of at least 0.05% by weight based on the weight of the polymer.

In a preferred embodiment of the present invention, a polymer is used which contains a small amount of a conventional delusterant such as titanium dioxide, barium sulfate, aluminum trioxide and the like. Such materials and the amounts employed are disclosed in United States Patent 2,205,722. Preferably at least 0.2%, and generally 1 to about 5% (by weight based on the weight of the polymer) of finely divided titanium dioxide is used for delustering purposes.

The invention will now be further described in the following specific examples which are to be regarded solely as illustrative and not as restricting the scope of the invention.

EXAMPLE I

A stainless steel autoclave is purged of air, filled with nitrogen and charged with an aqueous solution containing 75% by weight of hexamethylene diammonium adipate, 0.80 mole percent of hexamethylene diamine, 0.56 mole percent acetic acid, and 0.54% (based on the polymer weight) of sodium phenyl phosphinate in the form of an aqueous solution containing 25% by weight of the phosphinate. The autoclave is heated until its temperature is 195° C. at 250 p.s.i. pressure. Then an aqueous slurry containing 20% TiO_2 is added (2.0% TiO_2 based on the weight of polymer). The heating is continued until the temperature reaches 240° C. at 250 p.s.i. pressure. At this stage 0.02% (based on the polymer weight) of manganous hypophosphite in the form of a 10% aqueous solution is added. Heating is continued and at 242° C. bleeding off of water vapor is begun. The polymer polymerization cycle is continued as in Example 1 of United States Patent 2,163,636. Upon completion of the polymerization reaction, the molten polymer has a relative viscosity of 33.0 and a concentration of amine ends of 75 gram equivalents per 10^6 grams of polymer. The polymer is extruded in the form of a ribbon upon a casting wheel. After quenching, it is cut into chips suitable for remelting at the grid of a spinning assembly. The polyhexamethylene adipamide flake is melted in a steam atmosphere as taught in Waltz United States Patent 2,571,975 and is spun into a 70 total denier 34 filament yarn at a rate of 1350 yards per minute. The spinning is continued for a period of 2 days and the formation of spinning drips observed and recorded. The average time of drip-free spinning for this period is 11 hours. For a comparative control not containing the phosphinate compound this time is 2½ hours. For polyhexamethylene adipamide of comparable molecular weight wherein the concentration of amine end groups is 40 gram equivalents per 10^6 grams and which does not contain the phosphinate compound this time is about 6½ hours.

The example thus shows that the addition of the phosphinate compound reduces the frequency of spinning drips in dull polymer with increased amine end concentration to a value equal or less than the value prevailing for a polymer with low amine end group concentration.

The yarn is cold drawn and scoured according to conventional techniques. The product is a white yarn with superior dyeability.

EXAMPLE II

A stainless steel autoclave is charged with 464.0 pounds of an aqueous solution containing 52.02% by weight of hexamethylene diammonium adipate, 487 grams of aminopropyl morpholine (0.85 mole percent), 1280 grams of

an aqueous solution containing 25% by weight of sodium phenyl phosphinate (0.5% based on the polymer weight). The autoclave is purged of air, filled with nitrogen and heated until its temperature is 220° C. at 250 p.s.i. pressure. Then 91.0 grams of an aqueous slurry containing 20% TiO_2 is added (0.02% based on the weight of polymer). The heating is continued until the temperature reaches 240° C. at 250 p.s.i. pressure. At this stage, bleeding off of water vapor is begun. The polymer polymerization cycle is continued as in Example 1 of United States Patent 2,163,636. Upon completion of the polymerization reaction, the molten polymer has a relative viscosity of 35.1 and a concentration of amine ends of 114 gram equivalents per 10^6 grams of polymer. The polymer is extruded in the form of a ribbon upon a casting wheel. After quenching, it is cut into chips suitable for remelting at the grid of a spinning assembly. The polyhexamethylene adipamide flake is spun into a 30 total denier 10 filament yarn at a rate of about 1206 y.p.m. The spinning is continued for a period of 100 hours and the formation of spinning drips observed and recorded. The average time of drip-free spinning for this period is 25 hours. For a comparative control not containing the phosphinate compound this time is 12 hours. For polyhexamethylene adipamide of comparable molecular weight wherein the concentration of amine end groups is 40 and which does not contain a phosphinate compound this time is about 30 hours.

The example shows that the addition of the phosphinate compound reduces the frequency of spinning drips in bright polymer with increased amine end concentration to about the value prevailing for a polymer with low amine end group concentration.

The yarn is cold drawn and scoured according to conventional techniques. The product is a white, oxidation-resistant yarn with superior dyeability.

EXAMPLE III

A polyhexamethylene adipamide yarn is prepared following the procedure of Example I using 0.68 weight percent of sodium 2,5-dimethylphenylphosphinate. Essentially the same reduction in frequency of spinning drips is observed.

EXAMPLE IV

Preparation of Prepolymer of Poly(2-Methyl Hexamethylene Oxamide)

0.55 pound of sodium phenylphosphinate (0.5% based on the weight of polymer), 80.80 pounds of 2-methyl hexamethylenediamine (0.64 pound or 0.80 mol percent excess) and about 2.2 liters toluene are placed in a stainless steel autoclave, and stirred for about 20 minutes. Di-n-butyl oxalate in an amount of 124.5 pounds is then added together with 1.9 liters toluene. Fast stirring is maintained throughout the prepolymerization. Toluene is removed at the end of the prepolymerization by applying a vacuum.

Preparation of Polymer

The autoclave pressure is then reduced below 50 mm. mercury and the temperature raised to 270° C. The temperature is maintained between 270° C. and 275° C. for one hour to complete the polymerization. The polymer has an inherent viscosity of 1.0 and a concentration of amine end groups of 120 gram equivalents per 10^6 grams of polymer. The polymer is extruded in the form of a ribbon upon a casting wheel. After quenching, it is cut into flakes suitable for remelting in a screw melter. The poly(2-methyl hexamethylene oxamide) flake is melted in a screw melter maintained at 285° C. and spun into a 30 total denier 10 filament yarn at a speed of about 100 y.p.m. The average drip-free spinning time is approximately twice as long as for a comparative control of the same polymer having a concentration of amine end of 40 gram equivalents per 10^6 grams of polymer in which no phosphinate compound has been added.

EXAMPLE V

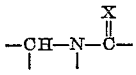
The salt of m-xylylene diamine and adipic acid is made by preparing an 11% by weight solution of adipic acid in methanol in a stainless steel container, and then adding an equimolar quantity of m-xylylene diamine in the form of a 67% by weight solution in methanol while stirring the solution vigorously. The stirring is reduced to a moderate rate and continued for 30 seconds after which the container is blanketed with nitrogen and allowed to stand without agitation for 3 hours. The salt is then filtered off and dried in a vacuum oven at a temperature of 80° C. The salt, in an amount of 2000 grams, is charged into a 5 pound capacity autoclave with 2000 grams of water. An additional 7.1 grams meta-xylylene diamine and 0.54% of sodium phenylphosphinate (based on the polymer weight) are added in the form of an aqueous solution containing 25% of the phosphinate. The temperature is raised to 200° C. and the pressure to 250 pounds per square inch and both are maintained for 60 minutes. The pressure is then reduced to atmospheric pressure and the temperature raised to 250° C. These conditions are maintained for a period of 30 minutes to provide a polyamide having an inherent viscosity of 1.10, and a concentration of amine ends of 100 gram equivalents per 10^6 grams of polymer.

The polymer is discharged from the autoclave and cut into flake as described in United States Patent 2,289,774. The flake is melt-spun to form 13 filament, 40 denier yarn in the conventional manner by extruding through a spinning pack of the type described in United States Patent 2,266,363 the temperature of the molten polymer being 250 to 270° C. The filaments are quenched and cold drawn in the conventional manner. The average drip-free spinning time is about twice that of a comparative control containing the same concentration of amine ends and no phosphinate compound. The resulting yarn has superior dyeability.

EXAMPLE VI

2000 grams of caprolactam are charged in an autoclave and heated above the melting point. In the molten caprolactam are dissolved 8.0 grams of hexamethylene diamine and 5.4 grams of sodium phenylphosphinate. The polymerization of the caprolactam is conducted by raising the temperature to 270° C. and the pressure to 250 p.s.i. and maintaining these conditions for 30 minutes. The pressure is next reduced to atmospheric and then to about 10 mm. mercury, which pressure is maintained for about 2 hours while the temperature is raised to and maintained at 270° C. The molten polymer is then discharged as a ribbon by extruding it from the autoclave through a narrow slot. The ribbon is quenched on a water-cooled casting wheel and cut into ½ inch flake. The polymer has 85 gram equivalents of amine end groups per 10^6 gram of polymer. A yarn is melt spun from the flake with low frequency of spinning drips, drawn and washed. The yarn shows superior dyeability to deep shades.

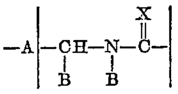
The synthetic linear fiber-forming polymers useful in the practice of the present invention are any of those which have the structural unit



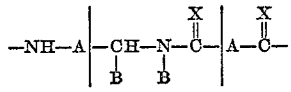
$$-\underset{|}{C}H-\underset{|}{N}-\overset{\overset{X}{\|}}{C}-$$

in at least 50% of the recurring units of the main polymer chain. Among the polymers which may be used are those containing the following recurring units.

Polyamides:

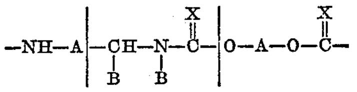


$$-A\left|-\underset{B}{\underset{|}{C}}H-\underset{B}{\underset{|}{N}}-\overset{\overset{X}{\|}}{C}-\right|$$



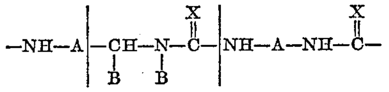
$$-NH-A\left|-\underset{B}{\underset{|}{C}}H-\underset{B}{\underset{|}{N}}-\overset{\overset{X}{\|}}{C}-\right|A-\overset{\overset{X}{\|}}{C}-$$

Polyurethanes:

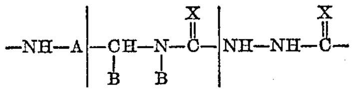


$$-NH-A\left|-\underset{B}{\underset{|}{C}}H-\underset{B}{\underset{|}{N}}-\overset{\overset{X}{\|}}{C}-\right|O-A-O-\overset{\overset{X}{\|}}{C}-$$

Polyureas:



$$-NH-A\left|-\underset{B}{\underset{|}{C}}H-\underset{B}{\underset{|}{N}}-\overset{\overset{X}{\|}}{C}-\right|NH-A-NH-\overset{\overset{X}{\|}}{C}-$$



$$-NH-A\left|-\underset{B}{\underset{|}{C}}H-\underset{B}{\underset{|}{N}}-\overset{\overset{X}{\|}}{C}-\right|NH-NH-\overset{\overset{X}{\|}}{C}-$$

wherein X is oxygen or sulfur, A is a divalent organic radical and each B is a monovalent organic radical including hydrogen. Representative groups of such polymers are disclosed in United States Patents Nos. 2,816,879; 2,731,446; 2,731,445; 2,313,871; 2,276,164; 2,276,160; 2,201,172; 2,130,948; 2,071,253; 2,071,251; and 2,071,250.

When using such polymers at least 50% and preferably 90% to 100% of the recurring units contain the structural unit hereinbefore set forth. Thus, copolymers may be used in the practice of this invention provided such copolymers have the high amine end groups and do not contain over 50% of other recurring structural units.

In the polymer the desired concentration of amine end groups may be obtained by adding an appropriate amount of a primary or secondary amine or polyamines. Suitable amines include: methyl amine, ethyl amine, propyl amine, isopropyl amine, hexamethylene diamine, piperazine, N-amino pentyl piperazine, N,N′-diaminopentyl piperazine, N-amino propyl morpholine and many others.

For a polyamide derived from a diamine and a diacid, simply employing a slight excess of the diamine reactant will effect the desired increase in concentration of amine end groups in the polymer. An appropriate amount of excess amine is between 5 and 180 gram equivalents per million grams of polymer and preferably between 10 and 120 gram equivalents.

The amine effecting the increase of amine end groups may be added before or at the beginning of the polymerization or during the early stages of the polymerization. In the melt polymerization of polycarbonamides the most convenient time for adding the amine is to the salt solution prior to evaporation of the solvent and prior to polymerization. The phosphinate compound should be added prior to heating the polyamide forming reactants to elevated temperature near the melting point of the polyamide. It is essential that it be added prior to the melt-spinning operation. Conveniently, it may be added to the salt solution before the beginning of the polymerization reaction.

Phosphorus compounds other than those of the examples which may be used for the same purpose include:

sodium phenylphosphinate,
hexamethylene diammoniumphenylphosphinate,
sodium 2-hydroxybutyl-2-phosphinate,
sodium 2,5-dimethylphenylphosphinate,
sodium p-methylphenylphosphinate,
sodium ethylphosphinate,
sodium isobutylphosphinate,
sodium 3-pentylphosphinate,
sodium cyclopentylphosphinate,
sodium cyclohexylphosphinate,
sodium 2-methylcyclohexylphosphinate,
sodium isooctenylphosphinate,
sodium isooctylphosphinate,
sodium n-octylphosphinate,
sodium styrylphosphinate,
disodium 1,6-hexyldiphosphinate,
sodium 3-hydroxypropylphosphinate,
sodium 3-hydroxy-2-methylpropylphosphinate,
potassium 2-hydroxybutyl-2-phosphinate,
potassium 1-hydroxy-1-phenethylphosphinate,

sodium alpha-hydroxydiphenylmethylphosphinate,
sodium alpha-(n-butylamino)isopropylphosphinate,
sodium alpha-(2-phenethylamino)isopropylphosphinate,
potassium 3-hydroxy-2-methyl-propylphosphinate,
sodium 1-carboxypropyl-2-phosphinate,
sodium 4-carbomethoxybutylphosphinate,
sodium 4-cyanobutylphosphinate,
disodium 1,8-diaminooctyl-3,6-diphosphinate,
sodium 1,2-dicarboxyethylphosphinate,
sodium 1,4-dicarboxybutyl-2-phosphinate,
sodium 1,4-dicyanobutyl-2-phosphinate,
lithium phenylphosphinate,
potassium phenylphosphinate,
rubidium phenylphosphinate,
cesium phenylphosphinate,
magnesium phenylphosphinate,
calcium phenylphosphinate,
barium phenylphosphinate,
manganous phenylphosphinate,
aluminum phenylphosphinate,
stannous phenylphosphinate,
stannic phenylphosphinate,
potassium p-dodecylphenylphosphinate,
sodium p-dimethylaminophenylphosphinate,
potassium p-dimethylaminophenylphosphinate,
sodium p-(beta-carboxyethyl)phenylphosphinate,
tetramethylammoniumphenylphosphinate,
3-hydroxypropylphosphinic acid phostone,
3-hydroxy-2-methylpropylphosphinic acid phostone,
sodium o-methylphenylphosphinate,
sodium m-methylphenylphosphinate,
sodium o-ethylphenylphosphinate,
sodium m-ethylphenylphosphinate,
sodium 2,3-dimethylphenylphosphinate,
sodium 2,4-dimethylphenylphosphinate,
barium 2,5-dimethylphenylphosphinate,
sodium p-ethylphenylphosphinate,
sodium p-isopropylphenylphosphinate,
sodium p-methoxyphenylphosphinate, and
sodium p-bromophenylphosphinate.

The concentration of the phosphinate compound in the polymer should be at least 0.05% based on the weight of the polymer and preferably at least 0.2%. Amounts up to the limit of solubility in the polymer may be employed.

It has been found in accordance with this invention that the phosphinate compound makes possible melt spinning of the polymer with reduced frequency of drips and reduced requirements for wiping spinnerets. After spinning, the phosphinate compound may be removed from the yarn, if desired, by a scouring operation. The term "scouring" is used to signify a process whereby the yarn is contacted with a solvent for the phosphinate compound so that the phosphinate compound is partially or totally extracted from the yarn. Water or water containing a small amount of soap or detergent may be employed as the solvent.

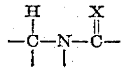
The process of this invention is applicable to polymers containing different concentrations of a delusterant (dull, semi-dull, and bright yarn). Since the spinning of dull yarns, in the absence of a phosphinate compound, frequently causes more spinning drips than the spinning of bright yarns, the advantages of the process of this invention are most pronounced when applied to delustered polymer.

The yarns obtained by the process of this invention are more deeply and uniformly dyeable at higher rate. They have specific utility in textile end uses where deep shades are desired, and in processes wherein high rate of dyeing is required, such as in slasher dyeing of warps.

Many modifications will be apparent to those skilled in the art from a reading of the above without a departure from the inventive concept.

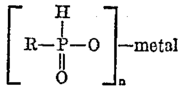
What is claimed is:

1. In a process for the formation of a filamentary structure of a synthetic linear fiber-forming polyamide containing in the main polymer chain a preponderance of recurring structural units of the formula



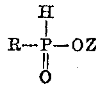
$$-\underset{|}{\overset{\overset{\displaystyle H}{|}}{C}}-\underset{|}{N}-\overset{\overset{\displaystyle X}{\|}}{C}-$$

wherein X consists of a member of the group consisting of oxygen and sulfur, and having from about 55 to 160 gram equivalents of amine end groups per 10^6 grams of polymer, by extruding the molten polymer through an orifice into a quenching medium, the improvement which comprises reducing the occurrence of drips during extrusion by dissolving in the extrudate prior to extrusion at least 0.05% by weight, based on the weight of the polymer, of a phosphorus compound selected from the group consisting of a compound of the formula



$$\left[R-\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle H}{|}}{P}}-O\right]_n-\text{metal}$$

and a compound of the formula



$$R-\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle H}{|}}{P}}-OZ$$

wherein

R is selected from the group consisting of alkyl, cycloalkyl, aryl and arylalkyl,

n is a whole number corresponding to the valence of the metal,

Z is selected from the group consisting of hydrogen, alkyl, aryl, arylalkyl, and alkyl substituted ammonium,

R and Z being alkylene when joined to form a ring structure.

2. The process of claim 1 wherein the polymer has from about 60 to 120 gram equivalents of amine end groups per 10^6 grams of polymer.

3. The process of claim 1 wherein the polymer contains at least 0.2% by weight, based on the weight of the polymer, of a finely divided delusterant.

4. The process of claim 3 wherein the polymer has from about 60 to 120 gram equivalents of amine end groups per 10^6 grams of polymer.

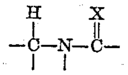
5. The process of claim 3 wherein the delusterant is titanium dioxide.

6. The process of claim 5 wherein the titanium dioxide is present in amounts of from about 1 to about 5%.

7. The process of claim 3 wherein the phosphorus compound is sodium phenylphosphinate.

8. The process of claim 3 wherein the phosphorus compound is sodium 2,5-dimethylphenylphosphinate.

9. The process of claim 3 wherein the polymer is a polycarbonamide and contains from 90–100% of



$$-\underset{|}{\overset{\overset{\displaystyle H}{|}}{C}}-\underset{|}{N}-\overset{\overset{\displaystyle X}{\|}}{C}-$$

groups wherein X is selected from the group consisting of oxygen and sulfur.

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