

SPECIFICATION

Removal of catalyst residues from polymers

This invention relates to the removal of catalyst residues from polymers.

Various polymerization reactions are described in the literature and the polymerizations are usually carried out in the presence of catalysts. One of the problems encountered with polymers prepared by such processes concerns the presence in the polymer of unacceptable levels of catalyst residues or ash-forming ingredients. The "ash content" of a product refers to catalyst constituents which are present in the polymer in unidentified form and which produce ash when the polymer is burned. The presence of these catalyst residues in the polymer adversely affects the color and heat stability of the polymer, as well as its electrical properties.

The ash or catalyst residue in polymers is typically occluded in the polymer particles. To reduce the level of this residue to acceptable levels, a solubilizing or complexing agent must be transported through the polymer to the catalyst. The catalyst is then solubilized and transported out of the polymer particle whence it can be separated from the polymer by filtration or washing. This catalyst removal is preferably carried out without the generation of undesirable side products such as hydrogen halides but if such halides are produced a suitable scavenging system for such halides can also be advantageously employed. The ease with which the purification steps occur is a function of the size, shape, and polarity of the solubilizing agent and of the solubilized catalyst. It is also a function of the catalyst activity.

Various treating methods have been proposed and tried by the prior art for the reduction of the level of such catalyst residues. For example, purification can be by treatment with anhydrous alcohols, alcoholic or aqueous solutions of acids, or complex forming organic compounds with a pretreatment in the presence of an alkylene oxide as disclosed in U.S. Patent 2,974,132. Alternatively, the polyolefin dispersion can be treated with an ether as disclosed in U.S. 3,045,002 and U.S. 3,083,192. Very satisfactory results have been obtained by the use of the combination of a dicarbonyl compound and an alkylene oxide as disclosed in U.S. 3,219,647.

In part, the combination of U.S. 3,219,647 is particularly advantageous because the alkylene oxide serves to scavenge the hydrogen halide evolved during the reaction of the treating agent with metal halides when such are present in the catalyst. This halide is most usually hydrogen chloride since the metal chlorides are usually employed as catalysts. HCl can lead to significant operating problems, especially in commercial equipment, in the nature of potential corrosion of conduits and vessels. Moreover with certain types of chelating agents such as the dicarbonyl compounds only moderate rates of extraction are obtained when they are used to sequester the catalyst residues in the absence of the alkylene oxide. Also, it is believed that at least in some instances the hydrogen halide may tend to inhibit the chelating reaction.

It has been found that alkylene oxides can function as deashing or treating agents. It has now been found however, that when only an alkylene oxide such as propylene oxide is used for deashing, long term commercial operations at the high reactor and contactor temperatures under olefin polymerizing conditions can result in plugging problems in the polyolefin recovery system. Analytical tests of the rubbery material causing the plugging problems revealed that *poly*-alkylene oxide was a major constituent in this material. The formation of this polymer can eventually result in recovery of polyolefins having increased levels of *poly*-alkylene oxides in the polymer product which can alter the polymer properties or processing. However, it has been found that in the presence of a dicarbonyl compound such as the conventional acetylacetone, formation of *poly*-alkylene oxide was inhibited suggesting that the dicarbonyl compound inhibited its formation. Accordingly another advantageous aspect of the combination of the dicarbonyl compound and the alkylene oxide may rest, at least in part, upon the synergistic or cooperating combination of an alkylene oxide which scavenges hydrogen halide produced with another complexing compound which inhibits the formation of *poly*-alkylene oxide.

It has now further been found that compounds of the types hereinafter set forth and described according to the instant invention effectively inhibit the formation of *poly*-alkylene oxide while constituting in combination with an alkylene oxide an effective deashing treatment for polyolefins.

In accordance with the instant invention, a method is provided for reducing a level of catalyst residues in a polymer prepared by catalytic polymerization in the presence of a catalyst system effective for said catalytic polymerization, said catalyst system having at least one component having at least one halogen atom which comprises contacting said polymer with a treating agent comprising in combination an alkyl monoether of a glycol, said alkyl monoether having an alkyl group having at least three carbon atoms, and an alkylene oxide as hereinafter described.

In one broad aspect, the invention is thus applicable to reduction of the level of catalyst residues from polymers prepared in the presence of a catalyst system having at least one halogen atom. In most instances, the halogen atom will be connected to at least one metal atom.

What constitutes an acceptable level of catalyst will vary depending on the catalyst system used, the polymerization system employed, and the uses to which the product will be placed. In the polymerization of polypropylene, for example, using titanium trichloride and DEAC, it is currently desirable to obtain purified polypropylene having no more than about 25 parts per million (ppm) titanium, about 75 ppm aluminum and no more than about 100 ppm each of ash and chlorides.

Titanium is believed to contribute color and chlorides can cause problems in corrosion and stabilization. To achieve these currently desirable levels without a deashing step would require a high activity catalyst. However, this invention is also considered applicable to such high activity catalyst systems if deashing becomes necessary to achieve levels of catalyst residues lower than what is currently considered acceptable, *i.e.*, the invention is not to be considered as limited by what are currently considered acceptable levels of catalyst residues.

Accordingly, in a further broad aspect the instant invention relates to polymers produced using a catalyst system wherein such a deashing step is necessary to achieve desirable levels of ash and other components.

The system used for removal of catalyst residues by the method of the present invention includes using as a treating or deashing compound an alkyl monoether of a glycol. The alkyl monoether of a glycol can comprise alkyl monoethers of glycols, said glycols conforming, for example, to the general formula

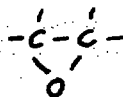


where R^1 is a hydrogen or a methyl group, r is an integer having a value of 1 or 2, and s is an integer having a value of 1, 2, or 3 in addition to glycols such as propylene glycol, dipropylene glycol and the like. Examples of such compounds include ethylene glycol (1,2-ethanediol), diethylene glycol (dihydroxydiethyl ether), triethylene glycol, propylene glycol (1,2-propanediol), and dipropylene glycol (2,2'-dihydroxydipropyl ether).

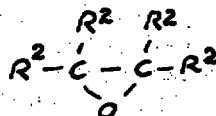
The alkyl group of the alkyl monoether of a glycol contains at least 3 carbon atoms and can be of a linear or branched nature. Generally said alkyl group contains from 3 to 8 carbon atoms. In a preferred embodiment, said alkyl group contains from 4 to 8 carbon atoms. Examples of specific compounds include the monobutyl-, mono-2-ethylhexyl- and monooctyl ethers of ethylene glycol and propylene glycol, the monobutyl-, mono-2-ethylbutyl-, mono-2-ethylhexyl-, and monooctyl ethers of dihydroxydiethyl ether (diethylene glycol) and dipropylene 1,2-glycol, and the monobutyl ethers of triethylene glycol. The monoalkyl ethers of dihydroxydiethyl ether (diethylene glycol) are a presently preferred group of compounds with the monobutyl ether of dihydroxydiethyl ether (diethylene glycol) particularly preferred because of its efficacy, stability, and low order of toxicity.

According to the present invention an alkylene oxide is used as a treating or deashing compound in combination with the monoether of a glycol for removing catalyst residues.

The alkylene oxides used in the present invention are compounds containing at least 2 carbon atoms and preferably containing from 2 to 8 carbon atoms and which include in their molecular structure at least one oxirane group having the structure



These compounds can be represented by the general formula:



wherein R^2 and R^3 each represent hydrogen, or an alkyl, cycloalkyl, or aryl group, including combinations thereof *e.g.*, alkylaryl and arylalkyl, or an epoxy-containing cyclic or alicyclic hydrocarbon group, with the proviso that the R^2 and/or R^3 groups can be joined to form carbocyclic group(s); said alkylene oxide containing a total of from 2—8 carbon atoms.

Typical compounds of this type include: epoxyethane, 1,2-epoxypropane, 1,2-epoxybutane, 2,3-epoxybutane, 1,2,3,4-diepoxycyclobutane, 1,2,4,5-diepoxypentane, 1,2,4,5,7,8-triepoxycyclooctane, 2,3-epoxy-2,3-dimethylbutane, 2,3-epoxy-2-methyl-3-ethylpentane, epoxyethylbenzene, epoxyethylcyclohexane, epoxyethyl-3,4-epoxycyclohexane, 1,2-epoxycyclohexane, 2,3-epoxyethylcyclohexane, 1,2-epoxycyclopentane, and the like.

A particularly preferred compound is 1,2-propylene oxide (epoxypropane) hereinafter sometimes referred to as propylene oxide.

The present invention is particularly advantageous for removal of catalyst residues as hereinafter disclosed when an alkyl monoether of a glycol as described above is used in connection with an alkylene oxide as described above as a treating or deashing agent to reduce the level of catalyst residues in a polymer product of a catalyst system which catalyst system is also effective for polymerization of the alkylene oxide.

Accordingly, in a preferred embodiment of the present invention, the alkyl monoether is used in

combination with the alkylene oxide as a combination purification system to reduce the level of catalyst residues in a polymer product.

The amount of alkyl monoether of a glycol used in the purification system broadly is an amount effective for removing catalyst residues and/or for inhibiting the formation of *poly*-alkylene oxide. The amount is at least 0.1 gram mole per gram atom of total metal in the catalyst system charged and can generally range from about 0.1 to about 15 gram moles per gram atoms of total metal in the catalyst system charged. Excellent results have been obtained when the alkyl monoether of a glycol is present in a range from about 1.5 to about 6 gram moles per gram atoms of total metal and more preferably in the range from about 1.5 to about 4 gram moles per gram atoms of total metal. The amount of alkylene oxide is an amount effective for scavenging halides produced during deashing treatment and/or for removing catalyst residues. The amount is at least 0.5 gram mole per gram atom of total halide in the catalyst system charged and can range generally from about 0.5 to about 20 gram moles per gram atom of halogen in the catalyst system charged. Excellent results have been obtained when the alkylene oxide is in the range of about 1 to 3 moles per gram atom of halide and more preferably about 1.5 to about 2.5 moles per gram atom of halide and these ranges are preferred for economy. When an alkyl monoether of a glycol and an alkylene oxide are used in combination the ratio of alkyl monoether of a glycol to alkylene oxide (calculated as the ratio of moles of the alkyl monoether employed per gram atom of total metal in the catalyst system charged to moles of alkylene oxide employed per gram atom of halide in the catalyst system charged) can range generally from about 0.1:1 to about 10:1. More preferably, the ratio of the alkyl monoether to the alkylene oxide is in the range of about 0.1:1 to about 4:1 and most preferably in the range of about 0.2:1 to about 3:1 or 1:1 to about 3:1 for excellent reduction of residual levels of ash and titanium. The alkyl monoether and/or the alkylene oxide can be introduced directly by themselves into the contactor or contact zone, or they can be added separately, or in combination in solution in an inert hydrocarbon.

The alkylene oxide is not a necessary component of a purification system if the sole and only object is to remove catalyst residues. However, in the combination of the present invention, the alkylene oxides are included to scavenge hydrogen halide formed in the reaction between metal halides and the alkyl monoether to minimize corrosion and other problems. Similarly, the alkyl monoether of the instant invention is not a necessary component of a purification system if the sole and only object is to remove catalyst residues. However, in the combination of the present invention, the monoalkyl ethers as herein described are included to inhibit the undesirable formation of *poly*-alkylene oxides which can cause plugging problems in the monomer recovery system or cause an increase in the level of the *poly*-alkylene oxides in the polymer product which can alter the polymer properties or processing.

The polymers which are treated in accordance with the present process are prepared, for example, from 1-olefins and/or conjugated diolefins. The present invention is particularly applicable to the treatment of polymers which are prepared by polymerizing 1-olefins because such polymerization systems often employ catalysts having at least one halide atom. Preferably, the 1-olefins most often used contain from 2 to 20 carbon atoms. Examples of such monomers include ethylene, propylene, 1-butene, 1-pentene, 3-methyl-1-butene, 1-hexene, 1-heptene, 1-octene, 4-methyl-1-pentene, 3-methyl-1-hexene, 1,3-butadiene, isoprene, 2,3-dimethyl butadiene, 2-methoxybutadiene, 1-eicosene, 4-ethyl-1-octadecene, 6-methyl-1-dodecene, 1,3-eicosadiene, 4,6-diethyl-1,3-decadiene, 4,5-dimethyl-1-cotene, 1-hexadiene and the like. This invention is particularly applicable to the treatment of polypropylene to remove catalyst residues. The polymers contemplated include homopolymers, copolymers, terpolymers, and the like. Representative polymers include polyethylene, polypropylene, poly(4-methyl-1-pentene), ethylene/propylene copolymers, ethylene/1-hexene copolymers, ethylene/1-decene copolymers, ethylene/1-butene/1,3-butadiene terpolymers, and the like. The invention is particularly applicable to the removal of catalyst residues from polypropylene and copolymers of propylene containing up to about 20 mole percent of ethylene or a higher 1-olefin.

This invention in one of its broad aspects is applicable to the treatment of polymers prepared by the use of catalyst compositions comprising at least one component having at least one halogen atom effective for polymerization of 1-olefins and/or conjugated diolefins. Frequently, such catalyst compositions include two or more components, for example, one of which may be a compound of a metal selected from Groups IV, V, VI, and VIII of the Periodic Table according to Mendeleev, and the second component being selected from organometal compounds, metal hydrides, and metals of Groups I, II, and III of the Periodic Table. Numerous examples of the catalyst compositions are well known in the art.

The compounds of a metal of Groups IV, V, VI, and VIII of the Periodic System include, for example, the oxides, hydrides, halides, oxyhalides and salts of organic acids, usually having twenty or less carbon atoms, such as formic acid, of the said groups of metals, such as titanium, zirconium, chromium, thorium, molybdenum and vanadium.

The compounds of a metal of Group IV of the Periodic System which can be employed can conform, for example, to the formula $MX_n(OR)_m$, where the sum $m + n$ equals the valence of the metal M, X is a halogen, and R is an organic radical usually having twenty or less carbon atoms, and preferably being an alkyl, cycloalkyl or aryl group or combinations, e.g., alkaryl and arylalkyl. Specific examples of such compounds are titanium tetrabutoxide (tetra-n-butyl titanate), tetra-sec-butyl titanate,

tetraisopropyl titanate, tetra-2-ethylbutyl titanate, tetra-2-ethylhexyl titanate, tetrastearyl titanate, tetraethyl titanate, tetra(chloroethyl)titanate, tetra-m-tolyl titanate, tetraallyl titanate, tetracyclohexenyl titanate, tetracyclopentyl titanate, tetraethyl zirconate, tetramethyl zirconate, tetraisopropyl zirconate, tetraamyl zirconate, dichloro diethyl titanate ($\text{Cl}_2\text{Ti}(\text{OC}_2\text{H}_5)_2$), monochloro-triethyl titanate ($\text{ClTi}(\text{OC}_2\text{H}_5)_3$) and the dichloro-diethyl zirconate ($\text{Cl}_2\text{Zr}(\text{OC}_2\text{H}_5)_2$). Also included are such compounds as $\text{Hf}(\text{OCH}_3)_4$, $\text{Th}(\text{OC}_3\text{H}_7)_4$, $\text{Th}(\text{OC}_4\text{H}_9)_4$, $\text{Cl}_3\text{Ti}(\text{OC}_6\text{H}_4\text{CH}_3)$, $\text{Zr}(\text{OC}_4\text{H}_9)_4$, $\text{Cl}_2\text{Hf}(\text{OC}_{10}\text{H}_{21})_2$, $\text{Th}(\text{OC}_6\text{H}_{13})_4$, and $\text{Zr}(\text{OC}_{12}\text{H}_{25})_4$.

Of particular interest are such catalysts employing a titanium compound. The titanium compound can be expressed, for example, as $\text{TiX}_p(\text{OR})_{4-p}$ in which R is (as above) a hydrocarbon group containing from 1 to about 20 carbon atoms such as alkyl, cycloalkyl, aryl, and combinations, e.g., alkaryl and arylalkyl, X is a halogen usually chlorine or bromine, and p is an integer in the range of 0 to 4 inclusive, provided that when p is zero at least one other component of the catalyst system has at least one halogen atom. Examples of specific compounds include titanium tetrachloride, titanium tetramethoxide, titanium tetracyclohexyloxide, titanium tetrabenzoyloxide, titanium chlorotrimethoxide, titanium dichlorodiethoxide, and titanium tribromo-n-butoxide, and mixtures.

Another suitable titanium compound is titanium trichloride which can be prepared by reduction of titanium tetrachloride with hydrogen, aluminum, or an organometal compound such as diethylaluminum chloride. One commercially available titanium trichloride of interest is produced by aluminum reduction of the tetrachloride and is a complex generally expressed as $\text{TiCl}_3 \cdot 1/3 \text{AlCl}_3$ or $3\text{TiCl}_3 \cdot \text{AlCl}_3$, hereinafter expressed as $3\text{TiCl}_3 \cdot \text{AlCl}_3$.

Some examples of the second component which can be employed with the metal compounds described above include trimethylaluminum, triethylaluminum, trisobutylaluminum, tri-n-butylaluminum, tri-n-pentylaluminum, trisooctylaluminum, tri-n-dodecylaluminum, triphenylaluminum, triethylgallium, triphenylgallium, tricyclohexylgallium, tri-n-butylindium, triethylthallium, diethylaluminum hydride, methylaluminum dichloride, dimethylaluminum chloride, ethylaluminum dichloride, dimethylaluminum chloride, di-n-butylaluminum bromide, isooctylaluminum diiodide, di-n-propylgallium fluoride, eicosylgallium dibromide, ditetradecylgallium fluoride, dicyclohexylgallium chloride, diphenylgallium bromide, diphenylindium chloride, dioctylindium fluoride, cyclohexylindium dibromide, 3-methylcyclohexylaluminum dichloride, 2-cyclohexylethylgallium dichloride, p-tolylberyllium iodide, di(3-phenyl-1-methylpropyl)indium fluoride, 2-(3-isopropylcyclohexyl)ethylthallium dibromide, and the like.

Some of the metal hydrides useful as the second component can include, as specific examples, aluminum hydride, lithium aluminum hydride, barium hydride, gallium hydride, indium hydride, sodium aluminum hydride, potassium beryllium hydride.

The metals of the first, second and third groups useful in the second component are applicable as a class, the most important members being sodium, magnesium and aluminum.

Of particular interest because of availability and efficacy are organoaluminum compounds which can be expressed as $\text{AlR}_b\text{Y}_{3-b}$ in which R is as above, Y is a monovalent radical selected from among the halogens and hydrogen, and b is an integer of 0 to 3. Examples of specific compounds include trimethylaluminum, tridodecylaluminum, tricyclohexylaluminum, triphenylaluminum, tribenzylaluminum, diethylaluminum chloride, ethylaluminum dichloride, isopropylaluminum dibromide, diisobutylaluminum hydride, and the like, and mixtures thereof.

A third catalyst component which can be used advantageously with the first and second components described above is an organic halide or metal halide where the organic radical is advantageously an alkyl, cycloalkyl or aryl group. In a preferred embodiment, the organic radical has thirty or fewer carbon atoms. Specific examples are ethyl bromide, ethyl trichloro titanium, 1-bromobenzene, cyclohexyl chloride. Also applicable are an alkali metal or ammonium halide, an aluminum halide (where the catalyst also includes another metal compound such as a titanium compound), a halogen, a hydrogen halide, a complex hydride, a mixture of an organic halide and a metal, and Grignard reagent.

A still more specific subgroup of catalysts where excellent color and low ash content are obtained by the practice of the invention include catalysts where an organometal compound is used in combination with a metal salt. The ratios of the catalyst compounds in a catalyst system can vary widely, depending upon the particular charge used and operating conditions, say from 0.02 to 50 mols of the first component per mol of the second catalyst component. If a third component is present, the amount can vary from 0.02 to 50 mols per mol of the second component.

Examples of some suitable catalyst systems in accordance with the foregoing disclosure are as follows:

(a) Aluminum trialkyls, e.g., triethylaluminum or trisobutylaluminum and the tetravalent metal halides of the type represented by titanium tetrachloride;

(b) An organic halide (such as ethyl bromide), a Group IV inorganic halide (such as titanium tetrachloride) and a low valence metal selected from the group consisting of alkali metals, beryllium, magnesium, zinc, cadmium, mercury, aluminum, gallium, indium and thallium, for example, magnesium, ethyl bromide and titanium tetrachloride, as such, or with the addition of metallic aluminum;

(c) A Group IV halide, for example, titanium tetrachloride, and a low valence metal identified in (b), for example, sodium or magnesium;

(d) A mixture of titanium hydride and an aluminum alkyl halide, *i.e.*, a mixture of titanium hydride and ethylaluminum sesquichloride;

(e) An organoaluminum halide such as diethylaluminum chloride and a trivalent metal halide such as titanium trichloride;

(f) A mixture of molybdenum pentachloride and organometal compounds and halides exemplified by triethylaluminum and ethylaluminum dichloride;

(g) A mixture of complex metal halides, exemplified by potassium fluotitanate, and an organometal compound and halides exemplified by triethylaluminum and diethylaluminum chloride;

(h) A mixture of a derivative selected from the oxides of molybdenum, alkali metal and ammonium molybdates, and an organometal halide exemplified by isobutylaluminum dichloride;

(i) A mixture of: a derivative of iridium, platinum and osmium selected from the group consisting of halides, oxides and complex compounds of iridium, platinum and osmium, said complex compounds corresponding to the formula $M'_x M''_y X_z$, wherein M' is an alkali metal or an ammonium radical, M'' is iridium, platinum or osmium, X is a halogen, and y is at least 1 and the sum of x and y is equal to the valence of M'' ; and a metallic organic compound exemplified by triethylaluminum, for example, iridium chloride and triethylaluminum or ethylaluminum sesquichloride;

(j) A mixture of a derivative of a metal selected from the group consisting of halides, oxyhalides, hydroxyhalides, oxyhydroxyhalides of a metal selected from the group consisting of molybdenum, tungsten, uranium, selenium, and tellurium, and complex salts of said halides and said oxyhalides with a member selected from the group consisting of halides of sodium, potassium, lithium, rubidium, cesium and ammonia and an organometal compound exemplified by triethylaluminum, for example, molybdenum pentachloride and ethylaluminum dichloride;

(k) A chromyl halide and at least one of the following (1) a metal hydride or an organometal compound, (2) an organometal halide and (3) a mixture of an organic halide and a metal, for example, chromyl chloride, ethyl bromide and magnesium;

(l) A titanium derivative, a complex hydride, and a halide of aluminum; for example, tetrabutyl titanate, lithium aluminum hydride, and aluminum chloride;

(m) At least one halide of titanium, zirconium or hafnium and at least one hydride of lithium, sodium, potassium, rubidium, cesium, magnesium, calcium, strontium, barium, lanthanum or thorium, for example, zirconium tetrachloride and calcium hydride;

(n) (1) A hydrocarbon derivative of one of the metals, zinc, cadmium, mercury, and magnesium and (2) a member selected from the group consisting of halides of titanium, zirconium, vanadium and molybdenum, oxyhalides of titanium, zirconium, vanadium, molybdenum and chromium, and complex salts of said halides and oxyhalides with a member selected from the group consisting of halides of the alkali metals and ammonia, for example, diethylzinc and titanium tetrachloride;

(o) (1) A tri- or tetrahalide of titanium, zirconium, hafnium and germanium, (2) an organophosphorus-containing compound and (3) at least one of the following (a) an organometal halide, (b) a mixture of an organic halide and a metal, and (c) a complex hydride, for example, triethylaluminum, titanium tetrachloride and a triphenyl phosphine;

(p) (1) A tri- or tetrahalide of titanium, zirconium, hafnium and germanium, (2) a peroxide of the formula $R''OOR''$ where R'' is hydrogen, alkyl, aralkyl, alkaryl, cycloalkyl, acyl, alkyne, or aryl, and (3) at least one of the following: (a) an organometal halide, (b) a mixture of an organic halide and a metal and (c) a complex hydride, for example, ethylaluminum sesquichloride, titanium tetrachloride and benzoyl peroxide;

(q) A tri- or tetrahalide of titanium, zirconium, hafnium and germanium, a metal alkoxide and at least one of the following: (1) an organometal halide, (2) a mixture of an organic halide and a metal, and (3) a complex hydride, for example, ethylaluminum sesquichloride, aluminum ethylate and titanium tetrachloride;

(r) (1) A halide of titanium, zirconium, hafnium or germanium, (2) a hydride selected from the group consisting of hydrides of aluminum, gallium, indium and thallium and complexes of said hydrides with alkali metal hydrides, and (3) an organic halide, for example, titanium tetrachloride, lithium aluminum hydride and ethyl bromide;

(s) (1) A halide of titanium, zirconium, hafnium, or germanium, (2) carbides and acetylenic compounds and (3) at least one of the following: (a) an organometal halide, (b) a mixture of an organic halide and a free metal, and (c) a complex hydride, for example, ethylaluminum sesquichloride, titanium tetrachloride and copper acetylide.

Although specific examples of catalyst systems have been provided to illustrate the applicability of the present invention, the invention is not limited thereto but is considered applicable for deashing polymers prepared by any catalyst system containing at least one halide atom.

One catalyst system which is preferred for use in the polymerization comprises a dialkylaluminum chloride and titanium trichloride, the latter compound preferably being prepared by reduction of titanium tetrachloride with aluminum. The reaction product thus prepared is a complex having the approximate formula $3TiCl_3 \cdot AlCl_3$. The reduction reaction can be carried out at an elevated temperature, for example, at a temperature in the range of 360 to 600°F, preferably from 375 to 450°F.

The amount of catalyst employed which is effective for polymerization can vary over a rather wide

range and will depend at least to a certain degree upon the particular catalyst system utilized. However, the determination of the actual amount of the catalyst employed in any particular polymerization is well within the skill of the art. In general, the mole ratio of the organometal compound to the metal halide falls within the range of 0.02 to 50.

5 Although not essential, it is often desirable to carry out the polymerization in the presence of elemental hydrogen, for example, to control the molecular weight of the product. 5

In the preparation of polymers of monoolefins, a presently preferred procedure involves conducting the reaction in the presence of a catalyst comprising an alkylaluminum halide and a titanium trihalide, the temperature being maintained at a level such that the polymer is formed as a finely divided 10 solid. The reaction is conducted in a suitable reaction diluent. While various hydrocarbons can be used as diluents, it is generally preferred that the polymerization be conducted as a mass operation in which the unreacted monomer acts as the diluent. By whatever means the polymerization is conducted, conditions are preferably maintained such that the polymer is formed and recovered as a finely divided solid (particle form process). However, it is within the scope of the invention to be employed in 15 conjunction with other polymerization processes such as liquid phase or gaseous phase processes. 15

Broadly, the method of the instant invention comprises contacting the polymer under conditions effective for removal of impurities with amounts of treating agents according to the instant invention which are effective for removal of the impurities. When an alkyl monoether according to the instant invention is used in combination with an alkylene oxide, the amount of said monoether is preferably also 20 effective to inhibit polymerization of said alkylene oxide and the amount of said alkylene oxide is also effective to scavenge any hydrogen halide produced. 20

In the preferred practice of the invention the polymer is dispersed in solid state in a hydrocarbon diluent and treated in such dispersion, preferably under conditions such that the diluent remains in the liquid phase. In many instances it is convenient to conduct the polymerization using the liquid monomer 25 as the reaction diluent under conditions to provide a pulverulent solid polymer and treat the polymer for removal of catalyst in this diluent after termination of the polymerization. However, it is within the scope of the invention to replace the unreacted liquid monomer after polymerization has been terminated with another hydrocarbon material and conduct the extraction step therein. Other suitable hydrocarbon diluents include paraffinic and aromatic hydrocarbons in which a catalyst-deashing agent complex is 30 sufficiently soluble for effective deashing. Generally, paraffinic hydrocarbons, for example those containing from such as 3 to such as 7 carbon atoms per molecule, such as pentane, heptane, mixtures thereof, and the like, can be used. In any case it is important to prevent contact of the system with air, water, or moisture prior to and during the extraction step. Extraction will be conducted in a temperature range and for a period of time effective to reduce the undesired impurities to an acceptable level without 35 causing the polymer to be degraded. The time will vary with temperature, degree of mixing, etc., but will generally be from one minute to several hours, preferably 10 to 100 minutes. 35

The resulting polymer slurry may then be passed to a filter, wherein the treated solid polymer is separated from the diluent which now contains the catalyst residues. To remove any adhering liquid, the polymer is washed on the filter, removed, and dried.

40 In a preferred embodiment of the present invention, a polymer slurry which has been treated according to the present invention to extract catalyst residues then passes to a washing step wherein the solid polymer undergoes further purification comprising contacting the polymer particles countercurrently with a washing hydrocarbon which is maintained in the liquid phase, preferably the same olefin used in the polymerization. Various hydrocarbons such as aromatic and paraffinic 45 hydrocarbons in which a catalyst-deashing agent complex is sufficiently soluble for effective washing can be used. Generally, paraffinic hydrocarbons, for example, those containing from such as 3 to such as 7 carbon atoms per molecule, such as pentane, heptane, mixtures thereof, and the like, can be advantageously employed as the wash liquid, although, as stated, it is preferred to utilize the monomer in liquid phase for this purpose. 45

50 The treated effluent is removed from the treating zone to the washing zone for the purification step just described. The overhead or by-product stream recovered from the washing zone contains monomer, soluble polymers, catalyst residues and a small amount of solid polymer. This stream can be separated into its various components if desired and the purified monomer recycled. The bottom or product stream from the washing zone comprises a solid polymer substantially free of catalyst residues. 50

55 The present invention is particularly applicable to polymers such as polypropylenes, prepared by polymerization of propylene in the presence of a catalyst system comprising a complex of titanium trichloride represented by the approximate formula $3TiCl_3 \cdot AlCl_3$, together with diethylaluminum chloride, the polymerization being carried out at a temperature in the range between 100 and 180°F. While not essential, it is frequently desirable to conduct the polymerization in the presence of elemental hydrogen 60 charged to the reactor prior to or in combination with the monomer charge. 60

While the method of this invention is particularly useful in treating dispersions of solid polymers to remove catalyst residues, it can also be employed to advantage to treat polymers in solution. In many polymerization systems, the reactor effluent comprises polymer in solution in a hydrocarbon solvent. Such a solution can be passed to a treating vessel wherein the extracting agent of this invention is 65 added. The contact time is for a period effective to reduce the catalyst residues in the recovered polymer 65

to an acceptable level, which may be from a few minutes up to several hours.

The polymer is separated from the liquid phase and can be further purified, if desired, by washing.

A more comprehensive understanding of the invention can be obtained by referring to the following illustrative examples which are not intended, however, to be unduly limitative of the invention.

5 EXAMPLE I 5

Propylene was polymerized in a 3.8 liter stirred stainless steel reactor in liquid propylene at 70°C for 1 hour by employing a commercially available $3\text{TiCl}_3\cdot\text{AlCl}_3$ complex as catalyst, diethylaluminum chloride (DEAC) as cocatalyst (4.78 mmoles), and molecular hydrogen to control molecular weight of the product.

10 The reactor was conditioned for each run by charging it with 3 liters of n-heptane, heating the closed reactor at 175°C for 30 minutes, draining the n-heptane, purging residual n-heptane with propylene vapor and cooling the reactor to room temperature under propylene pressure. 10

The conditioned reactor was purged with propylene vapor, the DEAC was charged, followed by the catalyst and the reactor was closed. Hydrogen was then admitted followed by 3 liters of liquid 15 propylene. The mixture was heated to polymerization temperature, 70°C. The reactor was maintained liquid full during polymerization by the addition of liquid propylene as required. 15

Polymerization was terminated at the end of the desired time although stirring was continued and purification initiated by shutting off the flow of liquid propylene to the reactor and draining a small quantity of liquid propylene from the reactor leaving sufficient room for the purification system. The 20 desired quantity of purification agent was flushed into the reactor with liquid propylene. Purification temperature was 70°C. After the desired time the reactor was cooled to about 25°C and the solubilized catalyst residues flushed from the reactor with fresh propylene. Finally the reactor was drained and the polymer recovered for determination of residual ash and titanium content. Ash was determined by 20 burning a weighed amount of polymer and titanium was determined by X-ray fluorescence.

25 The purification compounds employed and the results obtained are given in Table I. The following abbreviations are used. 25

"PO" is propylene oxide

"MC" is monomethyl ether of diethylene glycol (methyl carbitol)

"EC" is monoethyl ether of diethylene glycol (ethyl carbitol)

30 "BC" is monobutyl ether of diethylene glycol (butyl carbitol) 30

"Productivity, g/g" is grams polymer per gram catalyst per hour

TABLE I
Purification of Polypropylene

Run (a) No.	Purification System				Mole Ratio BC/PO	Cat. Wt. g	Calc. Mole Ratio DEAC TiCl ₃	Polymer		Percent Removal Ash	Percent Removal Ti	Cat. Prod. g/g/hr
	Compound	Mole Ratio (b)	BC/PO	Time Min.				Yield g	Residue ppm			
									Ash	Ti		
1 (C)	none	—	—	—	0.1008	9.4	149	1460	161	(c) —	—	1480
2 (C)	MC	7.8	—	45	0.1115	8.5	159	1320	175	—	—	1430
3 (C)	"	16	—	90	0.1054	9.0	150	1520	170	—	—	1420
4 (C)	EC	6.8	—	45	0.1015	9.4	123	2090	170	—	—	1170
5 (C)	"	13	—	90	0.1086	8.7	180	670	95	54	45	1660
6 (C)	BC	5.3	—	45	0.1040	9.1	158	160	16	89	90	1520
7 (C)	"	11	—	90	0.1051	9.0	157	250	9	83	95	1490
8 (C)	PO	6.3	—	45	0.1069	8.9	184	130	24	91	86	1720
9 (C)	"	9.6	—	90	0.1161	8.2	173	180	24	88	26	1490
10 (C)	"	10	—	"	0.1009	9.4	151	250	21	83	88	1500
11 (C)	"	11	—	"	0.1025	9.3	169	110	17	92	90	1650
12 (I)	BC/PO	11/6.5	1.7:1	"	0.0979	9.7	132	130	25	91	86	1350
13 (I)	"	11/1.2	9.0:1	"	0.1167	8.1	158	240	11	84	94	1350
14 (I)	"	11/1.3	8.5:1	"	0.1170	8.9	132	150	11	90	"	1230

(a) C represents a control run; I represents an invention run.

(b) Mole ratio of MC, EC, and BC based on moles per gram atom of total metals; mole ratio of PO based on moles per gram atom of chloride; ratio BC/PO based on moles of BC based on moles per gram atom of total metal to moles of PO based on moles per gram of chloride. A dash signifies not applicable.

(c) In these columns, a dash indicates that a value was not determined.

Triphenyl phosphite added as catalyst adjuvant, 15 parts by weight per 100 parts by weight catalyst complex.

As the results of Table I show, when no purification agent is used as in control run 1, a high level of ash (1460 ppm) and high level of titanium (160 ppm) are found in the polymer. Control runs 2—5 indicate that the monomethyl- and monoethyl ethers of diethylene glycol are not effective as purification agents for polypropylene. In contrast, control runs 6 and 7 demonstrate that the monobutyl ether of diethylene glycol (BC) is particularly effective, even alone, in reducing the ash and titanium levels. It must be remembered that corrosive amounts of HCl forms as a product, however. Invention runs 12—14, demonstrate that mixtures of the monobutyl ether of diethylene glycol and propylene oxide provide an excellent purification system. Propylene oxide itself, as control runs 8—11 show, yields good results. However, it must be remembered that polypropylene oxide can be formed which can result in clogged recycle lines.

EXAMPLE II

The polymerization recipe employed was as follows:

n-hexane	100 milliliters (ml)
3TiCl ₃ .AlCl ₃	0.4 grams (g)
DEAC	0.909 g (5.0 ml, 25 wt. % in n-heptane)
propylene oxide	16.4 g (20 ml)
n-butyl carbitol	5.2 g (30.6 mmoles), when used

Into each 10-ounce (295 ml) bottle was charged the n-hexane. After purging the bottles with nitrogen, they were placed in a dry box and the DEAC and catalyst were added. The bottles were brought out, recapped, and the propylene oxide and n-butyl carbitol, if used, added. Each bottle was tumbled at 70°C for 4 hours in a bottle bath. On removal, the contents were poured into weighed aluminum pans to which was added methanol used to rinse out the bottles. No precipitate had formed in any of the bottles and only the control showed an increase in viscosity. Each pan was placed in a hood and the contents allowed to evaporate for 24—48 hours. The pans were then reweighed and the amount of residue determined.

The results are shown in Table II.

TABLE II

Preparation of Polypropylene Oxide (PPO)

Run No.	Recovered Weight, g	Initial Weight (a) g	Polymer (PPO)	
			Weight, g	Yield, %
15	3.64	1.31	2.33	14
16	6.86	6.51	0.35	2

(a) Catalyst + DEAC + BC (in run 16)

These data show that polypropylene oxide can be formed by contact with the catalyst system employed in polymerizing propylene and which can be present in the reactor effluent slurry treated with the purification system. Run 16 indicates that the presence of the monobutyl ether of diethylene glycol substantially reduces the formation of polypropylene oxide since only one-seventh (1/7) as much polymer formed as in control run 15 in the absence of the ether alcohol.

EXAMPLE III

Propylene was polymerized in liquid propylene in a continuous fashion by employing as the reactor a 15.2 cm diameter stainless steel pipe loop having a volume of 98.4 liters. The contents were continuously circulated by means of a pump. Catalyst was intermittently added in pulses (about 60/minute) and effluent intermittently taken off during each run. The catalyst consisted of 3TiCl₃.AlCl₃ of the type used in Example I and the cocatalyst was DEAC as a 25 wt. % solution in n-hexane. The concentration of DEAC varied from about 280 to 460 ppm based on the reactor contents as the mole ratio of DEAC to TiCl₃ was varied from about 3.2:1 to about 5.2:1. Triphenyl phosphite was added as a reactor adjuvant and molecular hydrogen was employed to control molecular weight of the

polypropylene produced. The average residence time during polymerization was 1.8 hours, the reactor temperature was 79°C, the propylene feed rate to the reactor was 48.8 liters/hour, and at steady state conditions the reactor was operated to provide 40 wt. % solids throughout all runs.

5 The reactor effluent was passed to the bottom of a 3-stage contactor column having a capacity of 58.6 liters and operated so that the upper stage was at 74°C, the middle stage was at 77°C, and bottom stage was at 78°C. 5

Deashing chemicals tested included n-butyl carbitol (BC) alone, propylene oxide (PO) alone, and a combination of the two. In these purification systems, one equivalent of the chemical used for Ti and Al removal is considered to be 3 moles of chemical per mole of combined Ti and Al compounds present.

10 One equivalent of the chemical used for chloride scavenging (propylene oxide) is considered to be one mole of chemical per mole of chloride present. Unless specified to the contrary, the chemical was added to the bottom (first) stage of the contactor. 10

The slurry leaving the contactor was then passed to a 15.2 cm diameter wash column where the catalyst residues solubilized in the contactor were washed from the slurry by a counter current flow of propylene at a temperature of 33°C and a rate of 1.6 kg liquid wash propylene per kg of polypropylene contained in the slurry. The top of the wash column was maintained at 63°C. 15

Polypropylene was recovered from the washed slurry leaving the wash column and stabilized with 0.0005 kg of 2,6-di-t-butyl-4-methylphenol per kg of polymer. The amount of ash and titanium in ppm of each polymer was determined as described in Example I.

20 The polymerization and contactor conditions employed and the results obtained are given in Table III. 20

TABLE III
Polymerization and Purification of Polypropylene

Run No.(a)	Mole Ratio DEAC		DEAC ppm	H ₂ Mole %	Purification System (Mole Ratios)			Contactor		H ₂ O In C ₃ Wash ppm	Cat. Prod. g/g (e)	Polymer Prod.		
	TiCl ₃	DEAC			PO (b)	BC (c)	BC/PO (d)	PO				Melt Flow ppm	Ash ppm	Ti ppm
								Input Wt. %	Output Wt. %					
17 (C)	3.99	424	0.10	7.0	0	—	0.47	0.14	30	2090	3.8	205	38	
18 (C)	4.28	419	.08	7.2	0	—	.47	.07	30	2430	1.5	320	52	
19 (C)	4.27	400	.11	16	0	—	.94	.50	30	2590	3.9	175	27	
20 (C)	4.19	426	.11	15	0	—	.94	.74	<1	2390	4.6	133	22	
21 (I)	4.43	422	.11	7.7	1.8	0.23	.47	.14	2.5	2190	5.5	100	15	
22 (I)	4.90	458	.11	13	3.7	0.28	.94	.35	2.5	2360	6.6	85	14	
23 (I)	4.59	427	.08	1.7	3.9	2.3	.10	.02	5	2540	4.0	120	16	
24 (I)	4.43	415	.08	1.7	3.9	2.3	.10	<.01	2	2490	1.7	60	13	
25 (I)	5.17	436	.08	1.7	2.1	1.2	.06	<.01	2	2690	1.9	90	14	
26 (I)	4.79	408	.08	1.7	3.6	2.1	.08	<.01	2	2490	1.8	85	10	
27 (I)	3.18	281	.08	2.0	6.0	3	.10	<.01	2	2620	1.7	90	12	
28 (I)	3.30	290	1.21	2.0	6.0	3	.10	<.01	1.5	2510	4.9	80	12	

(a) C represents a control run; I represents an invention run.

(b) Mole ratio based on moles per gram of chloride.

(c) Mole ratio based on moles per gram atom of total metals.

(d) Mole ratio with BC based on total metals, i.e., Ti and Al, and PO based on chloride.

(e) Productivity based on gram polymer per gram TiCl₃ per hour.

(f) BC to bottom stage of contactor, PO to top stage of contactor.

The triphenyl phosphite to ClCl₃ mole ratio was 0.15 to 1 for runs 17-22 and 0.20 to 1 for runs 23-28.

The results of control runs 17—20 indicate that propylene oxide is a fairly efficient purification agent when used alone, particularly, if low levels of water are present in the wash propylene (note run 20 vs. runs 17—19). Although no polypropylene oxide was detected in either the slurry leaving the contactor or in the recovered polypropylene in these tests it must be remembered that it was formed in tests with the commercial unit and that its presence resulted in line plugging problems.

The results of invention 21—28 indicate that the BC/PO system is effective in catalyst deashing. The results of run 24 shows that feeding BC to stage one of the contactor and PO to stage 3 of the contactor is no more effective than feeding both agents to stage one. The amount of titanium in the product is consistently low even when less than one equivalent (3 moles) of the monobutyl ether of diethylene glycol (BC) is used per mole of aluminum and titanium present in the reactor effluent. In terms of mole ratios of BC to PO (defined as the ratio of the moles of monobutyl ether to gram atoms of total metal in the catalyst charged to moles of propylene oxide per mole of chloride in the catalyst charged), invention runs 21—28 show that excellent reduction of ash and titanium is achieved from about 0.2:1 to about 3:1. Ash content in run 23 was higher than expected for no apparent reason.

A comparison of runs 24 to 28 of Example III to runs 12 to 14 of Example I indicate that addition of relatively large amounts of butyl carbitol in runs 12 to 14 was no more effective than the relatively smaller amounts employed in runs 24 to 28. Accordingly, amounts in ranges indicated by runs 24 to 28 are presently preferred, although amounts and ratios outside those ranges are also functional.

CLAIMS

1. A method of treating polymers prepared by polymerisation of a monomer or monomer mixture in the presence of a polymerisation catalyst composition containing one or more halogenated components, and one or more metal-containing components, which may be the same as or different from the halogenated component, to reduce the level of catalyst residues therein, which comprises contacting the polymer with a) an alkylene oxide in an amount of at least 0.5 gm. mole per gm. atom of total halide in the catalyst composition and b) an alkyl monoether glycol in an amount of at least 0.1 gm. mole per gram atom of total metal in the catalyst composition, the alkyl group in said alkyl monoether glycol containing at least three carbon atoms.

2. A method according to claim 1, wherein component b) is an alkyl monoether of a glycol of the formula:



wherein

R¹ is hydrogen or methyl;

r is 1 or 2; and

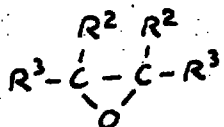
s is 1, 2, or 3.

3. A method according to claim 2, wherein component b) is an alkyl monoether of ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, or dipropylene glycol.

4. A method according to claim 1, 2 or 3, wherein component b) is an alkyl monoether glycol containing from 4—8 carbon atoms in the alkyl group.

5. A method according to claim 4, wherein component b) is a monobutyl-, mono-2-ethylhexyl- or monooctyl-ether of ethylene glycol or propylene glycol, a monobutyl-, mono-2-ethylbutyl-, mono-2-ethylhexyl- or monooctyl ether of dihydroxydiethyl ether (diethylene glycol) or dipropylene-1,2-glycol, or the monobutyl ether of triethylene glycol.

6. A method according to any one of the preceding claims, wherein component a) is an alkylene oxide of the formula



wherein R² and R³ each represent H, or an alkyl, cycloalkyl or aryl group or a combination thereof such as alkaryl or arylalkyl, or an epoxy-containing acyclic or alicyclic hydrocarbon group, with the proviso that the R² groups and/or the R³ groups may also be joined together to form carbocyclic group(s), said alkylene oxide containing a total of from 2—8 carbon atoms.

7. A method according to claim 6, wherein component a) is epoxyethane, 1,2-epoxypropane, 1,2-epoxybutane, 2,3-epoxybutane, 1,2,3,4-diepoxybutane, 1,2,4,5-diepoxy-pentane, 1,2,4,5,7,8-triepoxy-octane, 2,3-epoxy-2,3-dimethylbutane, 2,3-epoxy-2-methyl-3-ethylpentane, epoxyethylbenzene, epoxyethylcyclohexane, epoxyethyl-3,4-epoxycyclohexane, 1,2-epoxycyclohexane, 2,3-epoxyethyl-cyclohexane or 1,2-epoxycyclopentane.

8. A method according to any one of the preceding claims, wherein the polymer is treated with said alkylene oxide in an amount of from 0.5 to 20 gm moles of alkylene oxide per gm atom of halogen in the original catalyst composition.

9. A method according to any one of the preceding claims, wherein the polymer is treated with said alkyl glycol monoether in an amount of from 0.1 to 15 gm moles of alkyl glycol monoether per gm



The results of control runs 17—20 indicate that propylene oxide is a fairly efficient purification agent when used alone, particularly, if low levels of water are present in the wash propylene (note run 20 vs. runs 17—19). Although no polypropylene oxide was detected in either the slurry leaving the contactor or in the recovered polypropylene in these tests it must be remembered that it was formed in tests with the commercial unit and that its presence resulted in line plugging problems.

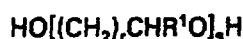
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A comparison of runs 24 to 28 of Example III to runs 12 to 14 of Example I indicate that addition of relatively large amounts of butyl carbitol in runs 12 to 14 was no more effective than the relatively smaller amounts employed in runs 24 to 28. Accordingly, amounts in ranges indicated by runs 24 to 28 are presently preferred, although amounts and ratios outside those ranges are also functional.

CLAIMS

1. A method of treating polymers prepared by polymerisation of a monomer or monomer mixture in the presence of a polymerisation catalyst composition containing one or more halogenated components, and one or more metal-containing components, which may be the same as or different from the halogenated component, to reduce the level of catalyst residues therein, which comprises contacting the polymer with a) an alkylene oxide in an amount of at least 0.5 gm. mole per gm. atom of total halide in the catalyst composition and b) an alkyl monoether glycol in an amount of at least 0.1 gm. mole per gram atom of total metal in the catalyst composition, the alkyl group in said alkyl monoether glycol containing at least three carbon atoms.

2. A method according to claim 1, wherein component b) is an alkyl monoether of a glycol of the formula:



wherein

R¹ is hydrogen or methyl;

r is 1 or 2; and

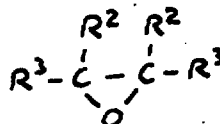
s is 1, 2, or 3.

3. A method according to claim 2, wherein component b) is an alkyl monoether of ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, or dipropylene glycol.

4. A method according to claim 1, 2 or 3, wherein component b) is an alkyl monoether glycol containing from 4—8 carbon atoms in the alkyl group.

5. A method according to claim 4, wherein component b) is a monobutyl-, mono-2-ethylhexyl- or monooctyl-ether of ethylene glycol or propylene glycol, a monobutyl-, mono-2-ethylbutyl-, mono-2-ethylhexyl- or monooctyl ether of dihydroxydiethyl ether (diethylene glycol) or dipropylene-1,2-glycol, or the monobutyl ether of triethylene glycol.

6. A method according to any one of the preceding claims, wherein component a) is an alkylene oxide of the formula



wherein R² and R³ each represent H, or an alkyl, cycloalkyl or aryl group or a combination thereof such as alkaryl or arylalkyl, or an epoxy-containing acyclic or alicyclic hydrocarbon group, with the proviso that the R² groups and/or the R³ groups may also be joined together to form carbocyclic group(s), said alkylene oxide containing a total of from 2—8 carbon atoms.

7. A method according to claim 6, wherein component a) is epoxyethane, 1,2-epoxypropane, 1,2-epoxybutane, 2,3-epoxybutane, 1,2,3,4-diepoxypentane, 1,2,4,5-diepoxypentane, 1,2,4,5,7,8-triepoxyoctane, 2,3-epoxy-2,3-dimethylbutane, 2,3-epoxy-2-methyl-3-ethylpentane, epoxyethylbenzene, epoxyethylcyclohexane, epoxyethyl-3,4-epoxycyclohexane, 1,2-epoxycyclohexane, 2,3-epoxyethylcyclohexane or 1,2-epoxycyclopentane.

8. A method according to any one of the preceding claims, wherein the polymer is treated with said alkylene oxide in an amount of from 0.5 to 20 gm moles of alkylene oxide per gm atom of halogen in the original catalyst composition.

9. A method according to any one of the preceding claims, wherein the polymer is treated with said alkyl glycol monoether in an amount of from 0.1 to 15 gm moles of alkyl glycol monoether per gm.



of metal in the original catalyst composition.

10. A method according to claim 9, wherein said amount of alkyl glycol monoether is from 1.5 to 6 gm moles per gm atom of metal in the catalyst composition.

11. A method according to any one of the preceding claims, wherein said alkyl glycol monoether and said alkylene oxide are used in a ratio of from 0.1:1 to 10:1, wherein said ratio is calculated as the ratio of the moles of alkyl glycol monoether per gm atom of metal in the original catalyst composition to the moles of alkylene oxide per gm atom of halogen in the original catalyst composition.

12. A method according to claim 11, wherein said ratio is from 0.1:1 to 4:1.

13. A method according to claim 11, wherein said ratio is from 0.2:1 to 3:1.

14. A method according to any one of the preceding claims, wherein the polymer is in particle form and is treated in suspension in a hydrocarbon diluent with said alkylene oxide and said alkyl glycol monoether.

15. A method according to claim 14, wherein said diluent is an excess of monomer used in the polymerisation process.

16. A method according to any one of the preceding claims, wherein after treatment with said alkylene oxide and said alkyl glycol monoether the polymer is washed with a hydrocarbon liquid effective to remove from the treated polymer the products formed by the reaction of said alkylene oxide and said alkyl glycol monoether and said catalyst residues.

17. A method according to claim 16, wherein said washing hydrocarbon comprises a hydrocarbon having 3 to 7 carbon atoms.

18. A method according to claim 17, wherein said washing hydrocarbon is pentane, heptane or a mixture thereof.

19. A method according to any one of the preceding claims, wherein said polymer is a polyolefin derived from one or more 1-olefins having from 2 to 20 carbon atoms in the molecule.

20. A method according to claim 19, wherein said polyolefin is a polymer obtained by polymerisation in the presence of a catalyst system comprising as a first component, a compound of a metal from Group IV, V, VI or VIII of the Mendeleev Periodic Table and, as a second component, an organometal compound or metal hydride of a metal of Group I, II or III of the Periodic Table.

21. A method according to claim 20, wherein said first component of the catalyst system is an oxide, hydride, halide, oxyhalide of titanium, zirconium, chromium, thorium, molybdenum or vanadium, or a salt of such a metal with an organic acid of less than 20 carbon atoms.

22. A method according to claim 20, wherein said first component of the catalyst system is a compound of the formula



wherein

M is a metal from Group IV of the Periodic Table;

X is a halogen;

R is an organic radical having 20 or less carbon atoms; and the sum $m + n$ equals the valence of the metal.

23. A method according to claim 22, wherein said compound is titanium tetrabutoxide (tetra-n-butyltitanate), tetra-sec-butyl titanate, tetraisopropyl titanate, tetra-2-ethylbutyl titanate, tetra-2-ethylhexyl titanate, tetrastearyl titanate, tetraethyl titanate, tetra(chloroethyl)titanate, tetra-m-tolyl titanate, tetraallyl titanate, tetracyclohexenyl titanate, tetracyclopentyl titanate, tetraethyl zirconate, tetramethyl zirconate, tetraisopropyl zirconate, tetraamyl zirconate, dichloro diethyl titanate $(Cl_2Ti(OC_2H_5)_2)$, monochloro-triethyl titanate $(ClTi(OC_2H_5)_3)$, dichloro-diethyl zirconate $(Cl_2Zr(OC_2H_5)_2)$, $Hf(OC_2H_5)_4$, $Th(OC_3H_7)_4$, $Th(OC_4H_9)_4$, $Cl_3Ti(OC_2H_5)_3$, $Zr(OC_4H_9)_4$, $Cl_2Hf(OC_2H_5)_2$, $Th(OC_6H_{13})_4$ or $Zr(OC_{12}H_{25})_4$.

24. A method according to claim 20, wherein said first component of the catalyst system is a titanium compound of the formula



wherein:

R is a hydrocarbon group containing from 1 to 20 carbon atoms;

X is chlorine or bromine; and

p is 0 or an integer from 1 to 4 provided that if p is zero at least one other component of said

catalyst system has at least one halogen atom.

25. A method according to claim 24, wherein said titanium compound is a complex of the formula $3TiCl_3 \cdot AlCl_3$.

26. A method according to any one of claims 20—25, wherein the second component of the catalyst system is trimethylaluminum, triethylaluminum, triisobutylaluminum, tri-n-butylaluminum, tri-n-pentylaluminum, triisooctylaluminum, tri-n-dodecylaluminum, triphenylaluminum, triethylgallium, triphenylgallium, tricyclohexylgallium, tri-n-butylindium, triethylthallium, diethylaluminum hydride, methylaluminum dichloride, dimethylaluminum chloride, ethylaluminum dichloride, dimethylaluminum chloride, di-n-butylaluminum bromide, isooctylaluminum diiodide, di-n-propylgallium fluoride, eicosylgallium dibromide, ditetradecylgallium fluoride, dicyclohexylgallium chloride, diphenylgallium bromide,



diphenylindium chloride, dioctylindium fluoride, cyclohexylindium dibromide, 3-methylcyclohexyl-aluminum dichloride, 2-cyclohexylethylgallium dichloride, p-tolylberyllium iodide, di(3-phenyl-1-methyl-propyl)indium fluoride or 2-(3-isopropylcyclohexyl)ethylthallium dibromide.

27. A method according to any one of claims 20—25, wherein said second component of the catalyst system is aluminum hydride, lithium aluminum hydride, barium hydride, gallium hydride, indium hydride, sodium aluminum hydride or potassium beryllium hydride.

28. A method according to any one of claims 20—25, wherein said second component of the catalyst system is an organoaluminum compound of the formula



10 wherein

R is a hydrocarbon group of 1 to 20 carbon atoms,
Y is halogen or hydrogen, and
b is 0 or an integer of 1 to 3.

29. A method according to claim 20, wherein said catalyst system comprises, as a third component ethyl bromide, ethyl trichloro titanium, 1-bromobenzene, cyclohexyl chloride, an alkali metal halide, an ammonium halide or an aluminum halide.

30. A method according to claim 20, wherein said catalyst system is any one of the following:

(a) the reaction product of an aluminum trialkyl and a titanium tetrahalide;

(b) the reaction product of an organic halide, a Group IV inorganic halide, and a low valence metal selected from alkali metals, beryllium, magnesium, zinc, cadmium, mercury, aluminum, gallium, indium and thallium;

(c) the reaction product of a Group IV metal halide and sodium or magnesium;

(d) the reaction product of a mixture of titanium hydride and an aluminum alkyl halide;

(e) the reaction product of an organoaluminum halide and a trivalent metal halide;

(f) a mixture of molybdenum pentachloride and an organometal compound;

(g) a mixture of a complex metal halide and an organometal compound;

(h) a mixture of molybdenum oxide, an alkali metal or ammonium molybdate and an organometal halide;

(i) a mixture of a halide, oxide or complex of iridium, platinum or osmium, said complex corresponding to the formula $\text{M}'_x\text{M}''\text{X}_y$, wherein M' is an alkali metal or an ammonium radical, M'' is iridium, platinum or osmium, X is a halogen, and y is at least 1 and the sum of x and y is equal to the valence of M' , and a metallic organic compound;

(j) a mixture of halide, oxyhalide, hydroxyhalide or oxyhydroxyhalide of molybdenum, tungsten, uranium, selenium or tellurium or a complex salt of such a halide or oxyhalide with a halide of sodium, potassium, lithium, rubidium, cesium or ammonia, and an organometal compound;

(k) a mixture of a chromyl halide and one or more of the following: (1) a metal hydride or an organometal compound, (2) an organometal halide, or (3) a mixture of an organic halide and a metal;

(l) a mixture of a titanium derivative, a complex hydride and a halide of aluminum;

(m) a mixture of a halide of titanium, zirconium or hafnium and a hydride of lithium, sodium, potassium, rubidium, cesium, magnesium, calcium, strontium, barium, lanthanum or thorium;

(n) a mixture of a hydrocarbon derivative of zinc, cadmium, mercury or magnesium, and a halide of titanium, zirconium, vanadium or molybdenum, an oxyhalide of titanium, zirconium, vanadium, molybdenum or chromium, or a complex salt of such a halide or oxyhalide with an alkali metal or ammonium halide;

(o) a mixture of a tri- or tetrahalide of titanium, zirconium, hafnium or germanium, an organo-phosphorus-containing compound and an organo metal halide, a mixture of an organic halide and a metal or a complex hydride;

(p) a mixture of a tri- or tetrahalide of titanium, zirconium, hafnium or germanium, a peroxide of the formula $\text{R}''\text{OOR}''$ where R'' is hydrogen, alkyl, aralkyl, alkaryl, cycloalkyl, acyl, alkyne, or aryl, and an organometal halide, a mixture of an organic halide and a metal, or a complex hydride;

(q) a mixture of a tri- or tetrahalide of titanium, zirconium, hafnium or germanium, a metal alkoxide and an organometal halide, a mixture of an organic halide and a metal, or a complex hydride;

(r) a mixture of a halide of titanium, zirconium, hafnium or germanium, a hydride of aluminum, gallium, indium or thallium or a complex of such a hydride with an alkali metal hydride, and an organic halide;

(s) a mixture of a halide of titanium, zirconium, hafnium, or germanium, a carbide or acetylenic compound and an organometal halide, a mixture of an organic halide and a free metal, or a complex hydride.

31. A method according to claim 1, wherein the polymer is polypropylene obtained by polymerising propylene in the presence of a catalyst system comprising a titanium chloride complex of the formula $3TiCl_3 \cdot AlCl_3$ and diethylaluminum, and the catalyst residues are reduced by treatment of the polymer with 1,2-propylene oxide and the mono-butyl ether of diethylene glycol.

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