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(54) Title: METHOD OF REDUCING FORMATION OF PRECIPITATES IN SOLVENT RECOVERY SYSTEM

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(57) Abstract: A method of removing at least one inert reaction diluent and/or wash diluent from a waste stream from a catalyst precursor production unit, where the waste stream includes at least one reaction diluent or wash solvent, at least one titanium alkoxide, at least one magnesium alkoxide, and at least one alkanol by contacting the waste stream with a solubilization solvent, and then subjecting the resulting stream to distillation. The method prevents precipitation of solid titanium and magnesium containing species during distillation.
METHOD OF REDUCING FORMATION OF PRECIPITATES
IN SOLVENT RECOVERY SYSTEM

The present invention relates to a method of reducing precipitate formation in a solvent recovery system. The method enables more efficient recovery of the solvent, reduces formation of solid material in distillation column reboilers and related equipment in the solvent recovery system, and reduces the waste effluent from the system.

Various types of Ziegler-Natta catalysts useful for polymerizing \( \alpha \)-olefins are known. Recently titanium-based Ziegler-Natta catalysts include stereoregulating catalysts that have sufficient activity to avoid the need for extraction and deashing of the resulting polymer. These high activity catalysts typically are prepared from a solid compound (pro催化剂) that usually contains magnesium, titanium and halide moieties, a cocatalyst (usually an organoaluminum compound) and, when propylene is polymerized in particular, an external electron donor or selectivity control agent (SCA). The cocatalyst and selectivity control agent may be separated added components of the catalyst composition or a neutral ligand that is complexed with the pro catalyst.

A number of patents describe various mechanisms for preparing magnesium- and titanium-containing compounds that are useful as precursors for the production of pro catalysts that are ultimately useful in preparing catalysts for the polymerization of \( \alpha \)-olefins. Examples include

- US-A-5,247,032 among others. Precursors are compounds that are readily converted to a pro catalyst by chlorination and addition of an internal electron donor. Magnesium and titanium-containing pro catalysts are preferably formed by reacting the magnesium and titanium-containing precursor compound with a tetravalent titanium halide, and an electron donor. The resulting pro catalyst is separated from the reaction mixture as a solid, by filtration, optionally after precipitation, or recrystallization. Production of these precursors may also involve precipitating a solid composition from solution or otherwise forming a suspension and then recovering the solid precursor. For example, in a preferred embodiment, the precursor can be precipitated from a reaction mixture comprising an alkanol by distilling or otherwise removing the alkanol, and filtering the remaining suspension. The filtrate from the filtration typically contains a number of useful ingredients or components that require removal prior to reuse or disposal. For example, the reaction diluent used in making the precursor, such as a chlorinated hydrocarbon, is a valuable ingredient that can be recovered and recycled to the manufacturing unit.
It is known in the art to recover valuable by-products of pro catalyst manufacture by subjecting the waste stream to one or more distillations, in the presence or absence of additional solvents, to recover the valuable titanium components. US-A-5,242,549 and 5,948,212 both disclose processes of recovering titanium from the waste stream of a pro catalyst manufacturing process. These patents are not concerned with recovering an inert reaction diluent from the waste stream of a pro catalyst precursor production unit, nor do they address the problem of preventing the formation of precipitates in a separation unit used to recover valuable by-products from the waste stream of a precursor production unit.

It would be useful to recover the valuable by-products, and to remove environmental hazardous by-products from the waste stream of a precursor production unit. A known recovery mechanism is to convey the waste stream to a distillation unit for separation of components. However, distilling the waste stream of a precursor production unit employing an alkanol for selective precipitation of the precursor can cause precipitation of solid components, especially magnesium and titanium containing species, because any remaining alkanol that had dissolved these species in the waste effluent is driven off in the distillation. Precipitation of these species causes undesirable solids accumulation in distillation column reboilers, and other related equipment.

Thus, there exists a need to provide an efficient and effective method of recovering useful ingredients that typically are present in the waste stream from a catalyst precursor manufacturing unit. In addition, there exists a need to develop a method of making a catalyst precursor more economically by enabling reuse of valuable by-products or waste effluent, and efficient disposal of waste. There also exists a need to develop a process that prevents precipitation of solid components during distillation of a waste stream from a catalyst precursor production unit, while at the same time enabling efficient recovery of valuable components in the waste stream.

According to the present invention, there is provided a method of removing at least one inert reaction diluent and/or liquid wash diluent from a waste stream from a catalyst precursor production unit, the waste stream including at least one reaction diluent and/or liquid wash diluent, at least one titanium alkoxide, at least one magnesium alkoxide, and at least one alkanol. The at least one reaction diluent and/or liquid wash diluent can be removed by contacting the waste stream with a solubilization solvent, and then subjecting the resulting stream to distillation. Desirably, the solubilization solvent: (i) is present in an amount sufficient to maintain the solubility of residual titanium and magnesium alkoxide species; (ii) has a boiling point higher than that of the reaction diluent(s) and/or wash diluent(s); and optionally, but preferably (iii) does not form an azeotrope with the reaction diluent(s) and/or wash solvent(s).

In accordance with an additional feature of an embodiment of the present invention, there is provided a method of making a catalyst precursor that includes contacting at least one titanium alkoxide, at least one magnesium alkoxide, at least one alkanol, and at least one reaction diluent;
removing at least a portion of the alkanol to precipitate a solid titanium and magnesium containing precursor component, thereby forming a suspension of the precursor in the at least one reaction diluent; separating the solid titanium and magnesium containing precursor component from the suspension thereby forming a solid precursor component and a waste stream including at least one reaction diluent, at least one titanium alkoxide, at least one magnesium alkoxide, and at least one alkanol; contacting the waste stream with a solubilization solvent; and subjecting the resulting mixture to distillation. Desirably, the solubilization solvent: (i) is present in an amount sufficient to maintain the solubility of residual titanium and magnesium alkoxide species; (ii) has a boiling point higher than that of the reaction diluent(s), and optionally, but preferably, (iii) does not form an azeotrope with the reaction diluent(s).

In a final embodiment of the invention, the solid precursor compound is washed after recovery by forming a suspension thereof with a liquid wash diluent, separating the washed solid precursor compound from the suspension to form a solid precursor component and a wash, waste liquid stream that preferably includes at least one liquid, wash diluent, at least one titanium alkoxide, at least one magnesium alkoxide, and at least one alkanol; contacting the waste liquid stream with a solubilization solvent; optionally combining the wash, waste liquid stream with at least one waste liquid stream including at least one reaction diluent before or after contacting with the solubilization agent; and subjecting the resulting mixture to distillation. Desirably, the solubilization solvent: (i) is present in an amount sufficient to maintain the solubility of residual titanium and magnesium alkoxide species; (ii) has a boiling point higher than that of the reaction diluent(s) and/or wash liquid diluent(s); and optionally, but preferably (iii) does not form an azeotrope with the reaction diluent(s) and/or wash solvent(s).

FIG. 1 illustrates a preferred separation unit useful in the present invention.

The method of the present invention is particularly suitable for removing and recovering inert diluents and/or wash solvents from waste streams formed in the production of Ziegler-Natta procatalyst precursors containing titanium moieties. In a preferred embodiment, the solubilization solvent preferably is one that: (a) is capable of maintaining the solubility of any potential precipitates that otherwise would form without its addition; (b) has a boiling point higher than all of the light components removed by distillation; and optionally, but preferably, (c) does not form an azeotrope with any of the light component(s) of the waste stream.

Particularly preferred solubilization solvents are alkanols, diols and phenolic compounds meeting the requirements (a), (b) and optionally, but preferably (3). Examples include octanol, decanol and cresol. An especially preferred solubilization solvent is octanol.

The purpose of the solubilization solvent is to enable separation of the inert diluent and/or wash diluent or other light components of the waste stream without causing substantial precipitation of solids. By "substantial precipitation" it is preferred that the amount of precipitates formed is
reduced by at least 50 percent when compared to a waste stream with no added solubilization solvent. Most preferably, however, no precipitates are formed.

Distillation of the mixture that contains the waste stream from the catalyst precursor production unit plus the solubilization solvent results in separation of the hydrocarbon and/or halohydrocarbon diluent from most of the other mixture components including the separation solvent without the formation of insoluble components. Although the solubilization solvent may later be separated from the remaining mixture components, in preferred practice the solubilization solvent remains with the bottom mixture as it continues to waste or to further processing. The recovered reaction diluent and/or wash solvent may undergo further processing to remove any azeotropic co-solvents (for example, alkanols) via molecular sieve or other methods known to those skilled in the art. The benefit according to the invention is the reduction in volume of the remaining bottoms allowing further recovery of metal salts, or disposal and recovery of substantial quantities of the light components.

Any inert reaction diluent and/or wash diluent can be used in the process of the invention. The diluent preferably is a hydrocarbon diluent such as butane, pentane, hexane, heptane, octane, xylene, or toluene, or a halohydrocarbon such as methylene chloride, chlorotoluene, or chlorobenzene. Isooctane and isopentane are preferred hydrocarbon reaction diluents and wash diluents, and chlorobenzene is a preferred halohydrocarbon reaction diluent and wash diluent. Most preferably, the reaction diluent and wash diluent comprises a combination of isopentane and chlorobenzene. Such liquid substances are alternatively referred to herein as “light component(s)”.

The precipitated materials can form from the remaining components in the waste stream. The waste stream from a precursor production unit may contain, in addition to the above-mentioned diluent and/or wash solvent, titanium alkoxides, titanium halides, titanium halide alkoxides, magnesium alkoxides, magnesium halides, magnesium halide alkoxides, phenolic compounds, and alkanols. In addition, the waste stream may contain partially reacted components obtained by partial or incomplete reaction of the titanium alkoxides, titanium halides, titanium halide alkoxides, magnesium alkoxides, magnesium halides, magnesium halide alkoxides, phenolic compounds, and alkanols.

The titanium alkoxides preferably are titanium ethoxides, the titanium halides are titanium tetrachlorides, and the titanium halide alkoxides are titanium chloro ethoxides. The magnesium alkoxides preferably are magnesium ethoxides, the magnesium halide alkoxides preferably are magnesium chloro ethoxides, and the magnesium halides are trace amounts of magnesium and chlorine-containing species. Preferred alkanols and phenolic compounds are those preferred components discussed above with reference to the manufacture of the catalyst precursor.

Simple distillation of such waste streams results in the formation of substantial amounts of undesirable solid material, particularly in the distillation column reboilers. This solid material has
the undesirable consequence of coating column reboiler sections, clogging the system or otherwise reducing the throughput and/or heat transfer in the column bottoms. Without wishing to be bound by any theory, the present inventor believes that it is likely that attempts at simple distillation will cause volatile light components, particularly alkanols (such as ethanol) to distill overhead either azeotropically or otherwise with the desirable reaction diluent and/or wash solvent. This in turn is believed to reduce the solubility of the remaining titanium, magnesium and/or chloride containing species in the bottoms section of the distillation zone, which in turn results in the formation of the foregoing undesirable solid materials.

The process of the invention, in the preferred embodiment, comprises the addition of a separation solvent of higher boiling point to a product mixture comprising isopentane and/or chlorobenzene in mixture with at least some titanium alkoxide, titanium chloroalkoxide, magnesium alkoxide and/or magnesium chloroalkoxide, a phenolic compound and a alkanol. The process preferably is applied to mixtures containing a variety of alkoxide moieties, each alkoxide containing up to 4 carbon atoms inclusive. Most commonly, however, each alkoxide of the mixture to be separated is ethoxide. The resulting mixture, including the solubilization solvent preferably is passed to a distillation zone which produces a split wherein the reaction diluent or other light component (for example, chlorobenzene or isopentane) along with alkanols resulting from the precursor preparation (such as ethanol) are the distillate product and a bottoms product includes the remainder of the mixture, including solubilization solvent.

Any amount of solubilization solvent can be supplied to the waste product mixture. Preferably, enough solvent should be supplied to provide equivalent solid solubility to that of the light alcohol species (especially ethanol) in solution. There is no defined maximum amount, but for practical purposes, the quantity should be kept close to the minimum amount required to achieve solubility of solids under use conditions. This will limit the total amount of solubilizing solvent added which will eventually contribute to the total waste quantity, or to the total amount of solvent which would be later processed.

Suitable precursor production techniques to which the present process may be applied, include any known process involving the foregoing reagents. According to one suitable process, the procatalyst precursor is produced in a two-step synthesis initially involving the reaction of a magnesium alkoxide of the formula, Mg(OR)₂, and a titanium tetraalkoxide of the formula, Ti(OR)₄, in which R, independently each occurrence, is C₁₋₄ alkyl, with a phenol, or a halo-, C₁₋₅ alkyl-, C₁₋₅ alkoxy, or di(C₁₋₅ alkyl)amido- substituted phenol. Preferred alkoxides are methoxide, ethoxide, n-propoxide and n-butoxide. Preferably, OR each occurrence is ethoxide.

Preferably, the phenolic compound is selected from phenol or activating group-substituted phenols. The expression "activating group" as it is used in this context, denotes a ring carbon atom substituent free from active hydrogen atoms that is ortho-para directing relative to further aromatic
ring substitution and which is generally but not invariably electron donating. Specifically preferred activating groups include: methyl, ethyl, isopropyl, t-butyl, methoxy, ethoxy, butoxy, amylxoy, chloro, bromo, dimethylamino and diethylamino. Particularly preferred phenolic compounds useful as an initial reactant include phenol, p-cresol, o-cresol, 3-methoxyphenol, e-dimethylaminophenol, 2,6-dimethylphenol and 2,6-di-t-butyl-4-methylphenol. A particularly preferred phenolic compound is o-cresol.

The initial reaction typically takes place in an inert reaction diluent by contacting magnesium alkoxide, titanium alkoxide and the phenolic compound at an elevated temperature. Any reaction diluent that is inert towards the reactants and has a relatively high boiling point so as to be a liquid during the contacting stage can be used. Preferred diluents include chlorobenzene, toluene, xylene and isoctane. Chlorobenzene is particularly preferred. The temperature at which the ingredients are reacted typically is within the range of from 60°C to 130°C at a pressure sufficient to maintain the reaction mixture in a liquid phase. The initial product preferably is a complex of the formula (I):

\[ \text{Mg}_2\text{Ti} (\text{OR})_3 \text{X}_2 \]  

wherein R is as previously defined, and X is the phenolic anion derivative formed by removal of a proton from the corresponding phenolic compound reactant. This product usually is a clear solution in the reaction diluent employed in its production.

The initial complex then is preferably contacted with a magnesium halide alcohoholate, preferably a hexalcohololate, in which the alcohol moieties are of the formula ROH where R is as previously defined, and halide is preferably chloride or bromide, most preferably, chloride. The initial complex and the magnesium halide alcohololate are mixed in an inert reaction diluent that is the same as the diluent used in the production of the initial complex or is different by virtue of the addition of a co-diluent or by diluent exchange. Preferably, the diluent is the same and the second synthetic procedure comprises the addition of the magnesium halide alcohololate to the product mixture containing the initial complex.

The reactants preferably are contacted and heated at a relatively mild temperature, for example, up to 100°C, until a clear solution is obtained and then heated at a higher temperature, from 110°C to 140°C, for example, to remove by-product alkanol from the reaction mixture, typically as an azeotrope with a portion of the reaction diluent. This alkanol removal is accompanied by the formation of opaque, spheroidal particles and typically alkanol is removed until the production of such particles ceases.

The solid precursor materials then is separated from the reaction mixture by any suitable means, including but not limited to, decantation, filtration, and centrifugation. Preferably, the solid material is filtered, most preferably under the impetus of pressure. The filtered solids then can be washed at least once with one or more solvents, including but not limited to monochlorobenzene,
toluene, xylene, isopentane, and isooctane. These wash solvents then can be removed by any means, but preferably are removed by blowing an inert gas through the filter cake. The dried filter cake then can be subjected to drying to produce a dry procatalyst precursor, and the wash liquid combined with any waste diluent from the previous steps, if any.

Alternatively, the solid precursor materials can be separated from the reaction solution or slurry by any means capable of separating a solid from a liquid. For example, the mixture containing the magnesium and titanium-containing precursor of the present invention can produce the solid, substantially dry high activity olefin polymerization procatalyst precursor by conventional methods such as impregnation, spray drying or spray cooling. Spray drying processes are well known in the art and are described, for example, in US-A-5,034,361 and US-A-4,771,024. The solution containing the magnesium and titanium-containing precursor usually is passed through a suitable atomizer to produce a spray or dispersion of droplets of the liquid mixture, a stream of hot gas such as nitrogen is arranged to contact the droplets to evaporate the solvent and the resulting solid product is collected. Atomization of the solution typically takes place in the absence of water or oxygen and nozzle atomizers or spinning disk atomizers are usually employed.

The foregoing process, regardless of the method for recovering the solid precursor, results in generation of a waste stream containing magnesium alkoxide, titanium alkoxide, a reaction diluent or waste wash diluent and an alkanol by-product.

In another suitable technique, the procatalyst precursor can be produced by contacting a magnesium alkoxide, a titanium alkoxide, a titanium halide, a phenolic compound and an alkanol. Preferred alkoxide moieties correspond to the formula OR, wherein R is as previously defined. Preferred alkanols are compounds of the formula ROH wherein R is as previously defined. Preferred phenolic compounds are those that have been previously defined as well.

The foregoing reactants are preferably contacted in an inert reaction diluent. The diluent preferably is a hydrocarbon diluent such as isopentane, isooctane, cyclohexane, xylene, or toluene, or a halohydrocarbon such as methylene chloride, chlorotoluene, or chlorobenzene. Isooctane is a preferred hydrocarbon diluent and chlorobenzene is a preferred halohydrocarbon diluent. Highly desirable precursors result by combining the respective reagents in the following molar amounts:

\[ 3\text{Mg(OEt)}_2 + x\text{(Ti(OEt)}_4) + y\text{(TiCl}_4) + z\text{(o-cresol)} + n\text{EtOH} \]

wherein \( y \) is more than 0.1 but less than 0.8, preferably more than 0.3 but less than 0.5,
\( x + y \) is more than 0.2 but less than 3, preferably more than 0.5 but less than 2,
\( z \) is more than 0.05 but less than 3, preferably more than 0.1 but less than 2, and
\( n \) is more than 0.5 but less than 9, preferably more than 2 but less than 5.

The initial interaction of the reactants in the reaction diluent takes place in a non-gaseous state at a moderate reaction temperature. Suitable reaction temperatures are from 30°C to 120°C, preferably from 35°C to 90°C. This initial heating usually results in the formation of a generally
clear solution. This solution then can be heated to a higher temperature to remove alkanol, ethanol in the preferred embodiment, typically as an azeotrope with a portion of the inert diluent. The temperature of this second heating will depend in part on the boiling point of any azeotrope containing alkanol that is formed. Typical heating temperatures are from 70°C to 120°C, preferably from 85°C to 110°C. Removing the alcohol usually results in the formation of a procatalyst precursor in the form of solid opaque, spheroidal particles. This process of making the precursor is a most preferred embodiment of the invention since it will yield a waste stream that, when heated to recover the inert diluent, may and often will precipitate a solid component.

In another suitable technique for preparing a procatalyst precursor, a magnesium alkoxide, a titanium alkoxide and a phenolic compound are contacted at an elevated temperature in an inert diluent. Suitable magnesium alkoxides, titanium alkoxides and phenolic compounds are those previously defined for the earlier disclosed preparations.

The diluent preferably is a hydrocarbon diluent such as isopentane, isoctane, cyclohexane, xylene, or toluene, or even a kerosene fraction, or the diluent is a halohydrocarbon such as methylene chloride, chlorotoluene, or chlorobenzene. Isoctane is a preferred hydrocarbon diluent and chlorobenzene is a preferred halohydrocarbon diluent. The procatalyst precursor that results preferably corresponds to formula (II):

$$\text{Mg}_2\text{Ti}_n(\text{OR})_p(\text{X})_q$$  \hspace{1cm} (II)

wherein R and X are as previously defined;

$$0.5 \leq m \leq 2.0;$$
$$0 \leq p \leq 2.0, \text{ and}$$
$$n' = (6 + (4m) - p).$$

A more preferred procatalyst precursor corresponds to the formula (III):

$$\text{Mg}_2\text{Ti} (\text{OR})_pX_2$$  \hspace{1cm} (III)

wherein R and X are as previously defined.

Preferably, in this embodiment the compounds are contacted at an elevated temperature and at a pressure sufficient to maintain the reaction mixture in a non-gaseous state. Suitable temperatures are from 50°C to 110°C. The contacting usually is conducted in a suitable reactor and contact is facilitated by conventional techniques such as shaking, stirring or refluxing. Desirably sufficient magnesium alkoxide is provided so that the resulting solution of complex alkoxide compound has from 1 percent by weight to 6 percent by weight of magnesium. Highly desirably, the reagents include magnesium diethoxide and titanium tetraethoxide. The reagents are preferably combined according to the following molar amounts:

$$x' (\text{phenolic compound}) + y' \text{Mg(OR)}_2 + z' \text{Ti(OR)}_4,$$

wherein: $x'$ is a number from 0 to 2,
$$y'$$ is a number from 3 to 4.5, and

-8-
z' is a number from 0.5 to 1.5.

The product mixture that results is a solution whose viscosity varies from "runny" to viscous depending upon the particular diluent employed and the quantity thereof as well as the ratio of starting materials employed. A certain quantity of alkanol is believed to be formed in the process as a by-product by ligand exchange with the phenolic compound.

The procatalyst precursor can be recovered from the foregoing mixture by any suitable technique and separated from the liquid diluent thereby resulting in a waste stream.

Another technique for preparing a procatalyst precursor involves contacting a magnesium alkoxide, a titanium alkoxide, a titanium tetrahalide compound, and a borate ester in an alkanol containing diluent. Suitable, magnesium alkoxide, titanium alkoxides and alkanols are those described with respect to previous techniques for precursor formation. The halide moieties of the titanium tetrahalide preferably are chloride or bromide with chloride being particularly preferred. Preferably, the alkoxide moieties of both the magnesium alkoxide and the titanium alkoxide are all ethoxide.

The resulting precursor preferably corresponds to the following formula (IV):
\[
\text{Mg}_5\text{Ti}_2(\text{OR})_{14} \quad (\text{IV})
\]
wherein R is a previously defined, and is preferably ethyl.

The contacting of magnesium, titanium and boron compounds takes place in the presence of an alkanol containing diluent at an elevated temperature and at a pressure sufficient to maintain the reaction mixture in a non-gaseous state. The alkanol preferably but not necessarily corresponds to the alkoxide moieties of one or more of the reactants. Suitable reaction temperatures are from 20°C to 180°C, but preferably are from 50°C to 90°C. The contacting is conducted in a suitable reactor and is facilitated by conventional techniques such as shaking, stirring or refluxing. The reagents are combined in the following preferred molar quantities:

\[
3\text{Mg}(\text{OR})_2 + 2\text{Ti}(\text{OR})_4 + 1.5\text{B(OR)}_3
\]
wherein R is as previously defined. The product obtained is a crystalline alcoholate preferably corresponding to the formula (V):
\[
\text{Mg}_5\text{Ti}_2(\text{OR})_{14} \ n'(\text{ROH}) \quad (\text{V})
\]
wherein R is as previously defined, preferably ethyl, and

n' is a number of from 0 to 6.

In this method of preparation of the precursor, the trialkylborate preferably remains in the mother liquor and may contribute to solids formation upon distillation. The trialkylborate preferably is provided to the reaction mixture in an amount from 0.1 mole to 2 moles per mole of titanium, more preferably from 0.5 mole to 1 mole per mole of titanium. The magnesium alkoxide preferably is provided in an amount of from 0.5 mole to 4 moles per mole of titanium. Quantities of magnesium alkoxide from 1 mole to 2 moles per mole of titanium are preferred.
The resulting precursor compound is recovered from the product mixture by well known methods such as filtration or decantation. The alcoholate then is converted to the complex alkoxide compound by removal of alkanol (ethanol in the preferred embodiment). The alkanol can be removed by conventional procedures, normally by heating. A particularly satisfactory method for alkanol removal is by an azeotropic distillation with a hydrocarbon or halohydrocarbon solvent. Any hydrocarbon or halohydrocarbon in which the complex alkoxide compound is soluble and with which the alkanol forms an azeotrope can be used for this purpose. A particularly useful hydrocarbon is isooctane and a particularly useful halohydrocarbon is chlorobenzene. The azeotropic solvent typically is added in a molar quantity in excess of the alkanol present and the resulting mixture then is heated to remove the alkanol. The complex alkoxide compound that results forms a clear solution in the excess hydrocarbon or halohydrocarbon at the boiling temperature of the azeotrope. It may be crystallized by removal of alcohol from the mixture to form solid opaque, spheroidal particles. These solid particles then can be separated from the mixture in accordance with any of the previously disclosed procedures.

This waste liquid resulting from the procatalyst precursor production according to any of the foregoing techniques or from a washing process may be subjected to the method of diluent or solvent recover according to the present invention. Mixtures of one or more solubilization solvents may also be used in the separation process. Preferably, the normal boiling point of the solubilization solvent is higher than that of the diluent or other light component to be recovered.

The method of the invention is more particularly illustrated by reference to FIG. 1, where a waste liquid stream emanating from an olefin polymerization procatalyst precursor production unit is denoted by 1. More preferably, this waste liquid stream constitutes a complex mixture of an inert reaction diluent and/or wash diluent, titanium alkoxides, magnesium alkoxides, titanium halides, phenolic compounds, and alkanols. In practice, there may be more than one waste streams from a production unit, and multiple production units contributing to waste stream 1. For example, a first stream might contain predominately reaction diluent and a second stream might contain predominately a wash diluent. Each stream could be treated independently in the manner described herein or combined for treatment.

The process stream is combined with the solubilizing solvent (2) in a mixing zone (10) which may be a tank or may be direct mixing in a line or pipe of a polyolefin procatalyst precursor process waste stream (1). Once combined, the combined stream containing at least the waste stream and the solubilizing agent enters the distillation zone (20) from which an overhead stream (4), middle distillate stream (5) and bottoms stream (6) emanate. Additional recovered streams could be employed at the discretion of the operator. Downstream processes for impurity removal (such as molecular sieves) could be included for the exiting product streams (4) and (5). Exiting product streams (4) and (5) then may be recycled to the polymerization catalyst precursor production unit.
for reuse, or it may be stored and used for other purposes, or sold. The bottoms stream (6) includes a concentrated mixture, including the solubilization solvent added as stream (2) and the solids that otherwise would form a precipitate.

The skilled artisan will appreciate that overhead distillate stream (4) and middle distillate stream (5) may not be utilized under all operation conditions. For example, if isopentane is the diluent that is desired to be recovered, this diluent can be removed from the column via stream (4), which then can be subsequently treated to recover the isopentane. If monochlorobenzene is the diluent that is to be recovered, however, middle distillate stream (5) is employed. Skilled artisans are capable of determining whether one or both of streams (4) and (5) are required, depending on the nature of the components to be recovered from the waste stream.

The distillation zone (20) is shown as a single column, but could alternatively be multiple columns. A suitable column is a packed column of from 2 to 4 sections, each of which has multiple stages. Other types of multiple stage columns also are suitable, depending upon the composition of the waste stream, the potential precipitate, and the solubilization solvent to be employed. Typical operation of the distillation zone depends on the diluent to be recovered. For haloalkane recovery, such as chlorobenzene, the column may operate at about 11 psig (180 kPa) at the base and a temperature varying from 120°C at the top to 170°C at the bottom of the column. For hydrocarbon recovery, such as isopentane, the column may operate at about 35 psig (340 kPa) at the base and a temperature varying from about 67°C at the top to 172°C at the bottom of the column. Column pressure may be adjusted upward or downward, which a concurrent increase or decrease in the noted temperature profile. In actual operation, the process may employ pumps, reboilers, rectifiers and/or other mechanical features (not depicted) as will be apparent to one of ordinary skill in this art.

Examples

In laboratory testing of compounds which could act as a solubilizing solvent, a simulated waste stream comprising chlorobenzene, ethanol, titanium tetraethoxide and magnesium diethoxide was heated to allow the removal of volatile components and precipitation of solid material to occur. Samples of the resulting solid were then placed into vials and various potential solubilizing agents were added to determine their effectiveness in resolubilizing the precipitate. Those materials that satisfactorily caused the solid to redissolve at ambient conditions were: 2-propanol, ethylene glycol dimethyl ether, water, 2-methyl-1-propanol, 1-butanol, 2-methoxy ethanol, ethylbenzene, 1-hexanol, 2-methoxyethyl ether, 1,1,3,3-tetramethoxy propane, p-methylphenol, 1-octanol, 1,5-pentanediol, 1,1,3-trimethoxy propane. Moreover, the boiling points of such compounds are all in excess of the normal boiling point of chlorobenzene. These compounds accordingly constitute satisfactory solubilizing solvents for use in a process for recovery of chlorobenzene according to the invention.
CLAIMS:

1. A method of removing at least one inert reaction diluent and/or wash diluent from a waste stream from a catalyst precursor production unit, whereby the waste stream includes at least one reaction diluent and/or wash diluent, at least one titanium alkoxide, at least one magnesium alkoxide, and at least one alkanol, the process comprising:
   contacting the waste stream with a solubilization solvent; and
   subjecting the resulting stream to distillation,
   wherein the solubilization solvent: (i) is present in an amount sufficient to maintain the solubility of residual titanium and magnesium alkoxide species; and (ii) has a boiling point higher than the one or more reaction diluent(s) and/or wash diluent(s).

2. The method according to claim 1, wherein the solubilization solvent also does not form an azeotrope with the one or more reaction diluent(s) and/or wash diluent(s).

3. The method according to claim 1, wherein the reaction diluent and/or wash diluent is selected from the group consisting of hydrocarbon and halohydrocarbon compounds.

4. The method according to claim 3 wherein the reaction diluent and/or wash diluent is selected from a group consisting of butane, pentane, hexane, heptane, octane, xylene, toluene, methylene chloride, chlorotoluene, and chlorobenzene.

5. The method according to claim 4, wherein the reaction diluent and/or wash solvent is selected from the group consisting of isopentane, isoctane, and chlorobenzene.

6. The method according to claim 1, wherein the solubilization solvent is selected from the group consisting of alkanols, diols and phenolic compounds.

7. The method according to claim 6, wherein the solubilization solvent is octanol, decanol or cresol.

8. The method according to claim 7 wherein the solubilization solvent is octanol.

9. A method of making a catalyst precursor comprising:
   contacting at least a titanium alkoxide, a magnesium alkoxide, and an alkanol, and at least one reaction diluent;
removing a portion of the alkanol to precipitate a solid titanium and magnesium containing precursor component, thereby resulting in a suspension of the precursor in at least one reaction diluent;

separating the solid titanium and magnesium containing precursor component from the suspension to form a solid precursor component and a waste stream that includes at least one reaction diluent;

optionally washing and again separating the solid titanium and magnesium containing precursor component to form a solid precursor component and a second or combined waste stream that includes at least one wash diluent;

and recovering the one or more inert reaction diluent(s) and/or wash diluent(s) by contacting the waste stream(s) with a solubilization solvent, and subjecting the resulting stream(s) to distillation,

wherein the solubilization solvent: (i) is present in an amount sufficient to maintain the solubility of residual titanium and magnesium alkoxide-containing species; and (ii) has a boiling point higher than the one or more reaction diluent(s) and/or wash diluent(s).

10. The method according to claim 9, wherein the solubilization solvent also does not form an azeotrope with the recovered reaction diluent(s) and/or wash diluent(s).

11. The method according to claim 9, wherein the reaction diluent and/or wash diluent is selected from the group consisting of hydrocarbon and/or halohydrocarbon compounds.

12. The method according to claim 11 wherein the reaction diluent and/or wash diluent is selected from the group consisting of butane, pentane, hexane, heptane, octane, xylene, toluene, methylene chloride, chlorotoluene, and chlorobenzene.

13. The method according to claim 12, wherein the reaction diluent and/or wash diluent is selected from the group consisting of isopentane, isooctane, and chlorobenzene.

14. The method according to claim 9, wherein the solubilization solvent is selected from the group consisting of alkanols, diols and phenolic compounds.

15. The method according to claim 14, wherein the solubilization solvent is octanol, decanol or cresol.

16. The method according to claim 15, wherein the solubilization solvent is octanol.