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PROCESS OF PREPARING A FLUID RARE EARTH ALKOXYLATION CATALYST

The present invention relates to a process of preparing a rare earth catalyst useful in an alkoxylation process.

Background of the Invention

A large variety of products useful, for instance, as nonionic surfactants, wetting and emulsifying agents, solvent, and chemical intermediates, are prepared by the addition reaction (alkoxylation reaction) of alkylene oxides (epoxides) with organic compounds having one or more active hydrogen atoms. For example, particular mention may be made of the alkanol ethoxylates and alkyl-substituted phenol ethoxylates prepared by the reaction of ethylene oxide with aliphatic alcohols or substituted phenols of 6 to 30 carbon atoms. Such ethoxylates, and to a lesser extent corresponding propoxylates and compounds containing mixed oxyethylene and oxypropylene groups, are widely employed as nonionic detergent components of commercial cleaning formulations for use in industry and in the home. As another example, the addition reaction of propylene oxide with polyols provides intermediates for the preparation of polyurethane products.

An illustration of the preparation of an alkanol ethoxylate (represented by formula III below) by addition of a number (n) of ethylene oxide molecules (formula II) to a single alkanol molecule (formula I) is presented by the equation

159159



I II III

The present invention particularly relates to an alkoxylation reaction catalysed by the phosphate salts of one or more of the rare earth elements.

Alkylene oxide addition reactions are known to produce a product mixture of various alkoxylate molecules having different numbers of alkylene oxide adducts (oxyalkylene adducts), e.g. having different values for the adduct number n in formula III above. The adduct number is a factor which in many respects controls the properties of the alkoxylate molecule, and efforts are made to tailor the average adduct number of a product and/or the distribution of adduct numbers within a product to the product's intended service.

It is known that alcohol alkoxylate products having a narrow range alkylene oxide adduct distribution are preferred for use in certain detergent formulations (GB-A-1462134; Research Disclosure No. 194010). Narrow-range alcohol alkoxylates are also known to be particularly valuable as chemical intermediates in the synthesis of certain carboxylated alkyl polyethers (US-A-4098818) and of certain alkyl ether sulfates GB-A-1553561).

US-A-5057627 describes an alkoxylation process catalysed by phosphate salts of the rare earth elements. These catalysts were typically prepared by adding an aqueous solution of a rare earth compound such as lanthanum chloride to an aqueous sodium orthophosphate or H_3PO_4 solution. The resulting catalyst was a solid powder that was stable with a long shelf-life. However,

often the reaction mixture prepared by these catalysts led to an increase in the viscosity of the mixture to 1000 mPa.s (1000 centipoise) or more. US-A-5057627 also describes a process where an alkylphosphate is added to a lanthanum solution of 2-ethoxyethanol and NEODOL™ 23 Alcohol. Such a system may produce a lower viscosity mixture. However, these catalysts have a slow reaction time.

It is desirable to prepare a catalyst that provides a low viscosity reaction system with faster reaction time.

Summary of the Invention

In accordance with the present invention there is provided a process for the preparation of a fluid rare earth phosphate catalyst composition comprising:

a) providing a rare earth salt soluble in C_9-C_{30} active hydrogen containing organic compound at a temperature of less than 120°C;

b) adding and dissolving the rare earth salt in a C_9-C_{30} active hydrogen containing organic compound thereby producing a rare earth/organic solution; and

c) adding phosphoric acid to the rare earth/organic solution in a rare earth salt to phosphoric acid molar ratio in the range of 0.7:1 to 1.3:1 thereby producing the fluid rare earth phosphate catalyst composition.

In accordance with the present invention there is also provided a process for the preparation of alkylene oxide adducts of active hydrogen containing organic compounds, which comprises contacting an alkylene oxide reactant comprising one or more vicinal alkylene oxides with an active hydrogen containing reactant comprising

one or more active hydrogen containing organic compounds, in the presence of a catalytically effective amount of the fluid catalyst composition prepared by the process of the present invention described above.

In accordance with the present invention there is further provided a process for the preparation of alkylene oxide adducts of primary monohydric alkanols, which comprises:

a) providing a rare earth salt soluble in C_9-C_{30} primary monohydric alkanols at a temperature of less than 120°C;

b) adding and dissolving the rare earth salt in a C_9-C_{30} primary monohydric alkanol solution thereby producing a rare earth/alkanol solution;

c) adding phosphoric acid to the rare earth/alkanol solution in a rare earth salt to phosphoric acid molar ratio in the range of 0.7:1 to 1.3:1 thereby producing the fluid rare earth phosphate catalyst in the alkanol;

d) optionally adding a base that does not contain a Group 1 or Group 2 of the elements of the periodic table in an amount effective to adjust the pH of the catalyst in the alkanol to a pH in the range of 5 to 8; and

e) contacting an alkylene oxide reactant comprising one or more vicinal alkylene oxides and having 2 to 4 carbon atoms with the fluid rare earth phosphate catalyst in the alkanol, thereby producing the alkylene oxide adducts of primary monohydric alkanols.

In accordance with the present invention there is still further provided a process for the preparation of alkylene oxide adducts of active hydrogen containing

organic compounds, which comprises contacting an alkylene oxide reactant comprising one or more vicinal alkylene oxides with an active hydrogen containing reactant comprising one or more active hydrogen containing organic compounds, in the presence of a catalytically effective amount of the fluid rare earth phosphate catalyst prepared by the process comprising:

a) providing a rare earth salt soluble in the active hydrogen containing reactant at a temperature of less than 120°C;

b) adding and dissolving the rare earth salt in the active hydrogen containing reactant thereby producing a rare earth/organic solution; and

c) adding phosphoric acid to the rare earth/organic solution in a rare earth salt to phosphoric acid molar ratio in the range of 0.7:1 to 1.3:1 thereby producing the fluid rare earth phosphate catalyst.

Description of the Preferred Embodiments

It has now been found that the alkoxylation reaction carried out in the presence of the rare earth phosphate catalyst composition prepared by the process of the present invention decreases reaction time and is easier to handle.

In the process of the present invention, a fluid rare earth phosphate catalyst is prepared by the steps comprising a) providing a certain rare earth salt, b) adding and dissolving the rare earth salt in a C_9-C_{30} active hydrogen containing organic compound, preferably in a C_9-C_{30} primary mono-hydric alkanol or alkylphenol, more preferably in a C_9-C_{30} primary mono-hydric alkanol; then c) adding phosphoric acid to the rare earth/organic solution, or more preferably to the rare earth/alkanol

solution. It has been surprisingly found that the desirable catalyst composition can be prepared in the C_9-C_{30} active hydrogen containing organic compound without the presence of low molecular weight alcohol or alkoxides (carbon number of less than 8).

When the catalyst is prepared according to the present invention, the rare earth phosphate is substantially uniformly dispersed in the alkanol having an average particle size of less than 2 μm (microns), more preferably medium diameter particles are less than 1 μm (1 micron). The catalyst composition comprising the dispersed rare earth phosphate salt and the alkanol has a viscosity of less than 50 mPa.s (50 centipoise) and is fluid. The term "fluid" means having particles which easily move and change their relative position without a separation of the mass, and which readily yield to pressure.

As the terminology is used herein, the "rare earth" elements are those of atomic numbers 39 and 57 to 71, elements of the "lanthanum series" are those of atomic numbers 57 to 71; the "lanthanide" elements are those of atomic numbers 58 to 71. Traditionally, the lanthanum series has further been divided into the "cerium earth" group of atomic numbers 57 to 62, the "terbium earth" group of atomic numbers 63 to 66, and the "yttrium earth" group of atomic numbers 67 to 71 (so named not because yttrium is a member of the group, but because yttrium is found with these elements in nature).

In general terms, the catalyst for the process of the present invention comprises one or more of the phosphate salts of the rare earth metals. In one preferred embodiment, the catalyst comprises one or more

of the phosphate salts of the lanthanum series elements. In another embodiment, the catalyst comprises one or more of the phosphate salts of the lanthanide elements. In a further specific embodiment, the catalyst comprises one or more of the phosphate salts of the elements of the cerium earth group. In still another specific embodiment, the catalyst comprises a mixture of rare earth metal phosphate salts wherein the distribution of the rare earth elements substantially corresponds to that of a naturally occurring rare earth ore, for example, monazite, bastnasite, xenotime, gadolinite or euxenite.

The catalyst in a given application of this process suitably contains the phosphate salt(s) of either one or a mixture of the rare earth elements. In one respect, preference can be expressed for catalysts comprising in catalytically effective amount one or more of the phosphate salts of elements selected from the group comprising cerium, lanthanum, praseodymium, neodymium, yttrium, samarium, gadolinium, dysprosium, erbium and ytterbium. In another respect, catalysts comprising a catalytically effective amount of one or more of the phosphate salts of the cerium earth group elements are particularly preferred, while catalysts comprising a catalytically effective amount of one or more of the phosphate salts of elements selected from the group consisting of cerium and lanthanum are considered most preferred. In a further respect, preferred catalysts comprise a catalytically effective amount of one or more of the phosphate salts of lanthanum.

Natural mineral ores which serve as the commercial sources of the rare earth elements generally contain several of the elements. These ores are often refined without separating this mixture into distinct elements.

For this reason, the use in the present invention of mixtures of the phosphate salts of several rare earth elements may be preferred from the standpoint of availability and cost. Specific examples of suitable mixtures of rare earth elements include those known as bastnasite, monazite, xenotime, didymium, gadolinite and euxenite.

The rare earth salt useful to produce the fluid rare earth phosphate catalysts are soluble in the C_9-C_{30} primary mono-hydric alkanol at a temperature of less than 120°C. Such rare earth salts can be, for example, halides, nitrates or carboxylates of the rare earth elements. Some examples of salts include bromides, chlorides, nitrates, acetates and octoates.

The rare earth salt is dissolved in the C_9-C_{30} active hydrogen containing organic compound at temperatures in the range of ambient temperature up to 120°C to provide a rare earth/organic solution. The rare earth salt may optionally be dissolved in water prior to addition to the organic compound, or preferably alkanol, to dissolve the rare earth salt faster. However, this is not necessary, and it is preferably desirable to have as little water as possible in the rare earth/alkanol solution.

To this rare earth/organic solution, phosphoric acid is added slowly in a rare earth salt to phosphoric acid molar ratio in the range of from 0.7:1, more preferably from 0.9:1, to 1.3:1, more preferably 1.1:1, to produce the fluid rare earth phosphate catalyst composition. The phosphoric acid can be in any form including concentrated form or in an aqueous solution. The concentration is

preferably in the range of 50 percent to 80 percent by weight in aqueous solution.

The fluid rare earth phosphate catalyst can be optionally treated with a base in an amount to bring the pH of the catalyst composition in the range of 5-8 as long as the base does not interfere with the alkoxylation reaction. Such base typically does not contain a Group 1 or Group 2 element of the Periodic Table, such as Na^+, K^+, Cs^+, Ba^+, Mg^+, Ca^+, etc. Ammonium hydroxide is particularly preferred.

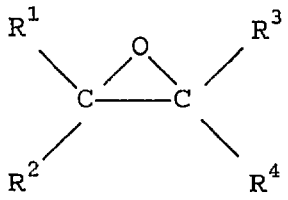
The resulting mixture should preferably be dried to a moisture content of less than 200 ppm prior to carrying out the alkoxylation reaction, to minimize polyalkylene oxide polymer formation.

The rare earth phosphate salt catalyst compounds are suitably characterised by the formula $(Lp\text{-}(PO_4)_q)_n$ wherein L is a rare earth element. As is well recognized in the art, the phosphate salts of the rare earth elements principally comprises rare earth elements in the trivalent states and have the formula LPO_4. However, the present invention is also intended to encompass divalent metal salts and tetravalent metal salts, in which case the subscripts p and q satisfy the relevant valency relationships, that is, when L is divalent p is 3 and q is 2, and when L is tetravalent p is 3 and q is 4. It is to be expected that generally the phosphate salt catalyst as prepared and as used in the present invention will consist essentially of compounds of the formula LPO_4. Further, the phosphate salt of rare earth elements may be in a dimer or trimeric form in which case n is 2 or 3 respectively.

In addition to a catalytically effective amount of the rare earth element compounds, the catalyst for the process of the present invention may also suitably contain other substances, including both those which may be introduced into the process as impurities in the phosphate salt catalyst as well as those which may be added to promote or modify catalyst activity.

The one or more of the phosphate salts of the rare earth elements are present in the reaction mixtures in a catalytically effective amount, i.e. an amount sufficient to promote the alkoxylation reaction or influence the alkylene oxide adduct distribution of the product. Although a specific quantity of catalyst is not critical to the present invention, preference may be expressed for use of the catalyst in an amount of at least 0.01 percent by weight (% w), while an amount between 0.02 and 5% w is considered more preferred and an amount between 0.1 and 2% w is considered most preferred for typical embodiments. These percentages are in terms of the weight of rare earth metal ions in the process mixture relative to the weight of active hydrogen containing compounds in that mixture. Substantially greater quantities of catalyst, e.g. up to 10% w, or more, are also very suitable. As a rule, the higher the desired average alkylene oxide adduct number of the alkoxylate product and the higher the desired rate of reaction, the greater the required quantity of catalyst.

The present invention is preferably applied to processes utilizing an alkylene oxide (epoxide) reactant which comprises one or more vicinal alkylene oxides, particularly the lower alkylene oxides and more particularly those in the C_2 to C_4 range. In general, the alkylene oxides are represented by the formula



wherein each of the R^1, R^2, R^3 and R^4 moieties is individually selected from the group consisting of hydrogen and alkyl moieties. Reactants which comprise ethylene oxide, propylene oxide, or mixtures of ethylene oxide and propylene oxide are more preferred, particularly those which consist essentially of ethylene oxide and propylene oxide. Alkylene oxide reactants consisting essentially of ethylene oxide are considered most preferred from the standpoint of commercial opportunities for the practice of alkoxylation processes, and also from the standpoint of the preparation of products having narrow-range ethylene oxide adduct distributions.

Likewise, the active hydrogen containing reactants suitably utilized in the process of the present invention include those known in the art for reaction with alkylene oxides and conversion to alkoxylate products. Suitable classes of active hydrogen containing reactants include (but are not necessarily limited to) alcohols, phenols, thiols (mercaptans), amines, polyols, carboxylic acids, and mixtures thereof. It is generally, but not necessarily, the case that the active hydrogen moiety of the reactant is of the form -XH wherein X represents either an oxygen, sulphur or (substituted, e.g. amino) nitrogen atom. Preference generally exists for use of hydroxyl-containing reactants. More preferably, the active hydrogen-containing reactant consists essentially of one or more active hydrogen containing compounds

selected from the group consisting of alkanols, alkyl polyols and phenols (including alkyl-substituted phenols).

Preference can also be expressed for the application of the present invention to the alkoxylation of primary active hydrogen containing compounds, that is, compounds wherein the active hydrogen moiety is attached to a primary carbon atom. As is often the case for alkoxylation reactions, such primary compounds are more reactive, and in some cases substantially more reactive, in the process of the present invention than are the corresponding secondary and tertiary compounds. Moreover, the present invention has been found to produce relatively broad-range alkylene oxide adduct distribution products when applied to secondary and tertiary active hydrogen containing reactants.

In the process to prepare the catalyst according to the present invention, the active hydrogen containing organic compound should be the reactant in the alkoxylation reaction. Thus, the active rare earth catalyst is produced "in-situ" of one of the reactants.

Among the suitable carboxylic acids, particular mention may be made of the mono- and dicarboxylic acids, both aliphatic (saturated and unsaturated) and aromatic. Specific examples include lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, rosin acids, tall oil acids and terephthalic acid. It has been observed that, as a rule, carboxylic acids undergo alkoxylation in the process of the present invention at a relatively slow rate.

Among the suitable amines, particular mention may be made of primary, secondary and tertiary alkylamines and

of alkylamines containing both amino and hydroxyl groups, e.g. N'N-di(n-butyl)-ethanol amine and tripropanolamine.

Among the suitable thiols, particular mention may be made of primary, secondary and tertiary alkane thiols having from 9 to 30 carbon atoms, particularly those having from 9 to 20 carbon atoms. Specific examples of suitable tertiary thiols are those having a highly branched carbon chain which are derived via hydrosulphurisation of the products of the oligomerisation of lower olefins, particularly the dimers, trimers, tetramers and pentamers of propylene and the butylenes. Secondary thiols are exemplified by the products of the hydrosulphurisation of the substantially linear oligomers of ethylene as are produced by the Oxo process. Representative, but by no means limiting, examples of thiols derived from ethylene oligomers include the linear carbon chain products, such as 2-decanethiol, 3-decanethiol, 4-decanethiol, 5-decanethiol, 3-dodecanethiol, 4-decanethiol, 5-decanethiol, 3-dodecanethiol, 5-dodecanethiol, 2-hexadecanethiol, 5-hexadecanethiol, and 8-octadencanethiol, and the branched carbon chain products, such as 2-methyl-4-tridecanethiol. Primary thiols are typically prepared from terminal olefins by hydrosulphurisation under free-radical conditions and include, for example, 1-dodecanethiol, 1-tetradecanethiol and 2-methyl-1-tridecanethiol.

The alcohols (both mono- and poly-hydroxy) and the phenols (including alkyl-substituted phenols) are preferred classes of active hydrogen containing reactants for purposes of the present invention. Among the phenols, particular mention may be made of phenol and alkyl-substituted phenols wherein each alkyl substituent has from 3 to 30 (preferably from 3 to 20) carbon atoms,

for example, p-hexylphenol, nonylphenol, p-decylphenol, nonylphenol and didecyl phenol.

Acyclic aliphatic mono-hydric alcohols (alkanols) form a most preferred class of reactants, particularly the primary alkanols, although secondary and tertiary alkanols are also very suitably utilized in the process of the present invention. Preference can also be expressed, for reason of both process performance and commercial value of the product, for alkanols having from 9 to 30 carbon atoms, with C_9 to C_{24} alkanols considered more preferred and C_9 to C_{20} alkanols considered most preferred, including mixtures thereof, such as a mixture of C_9 and C_{20} alkanols. As a general rule, the alkanols may be of branched or straight chain structure depending on the intended use. In one embodiment, preference further exists for alkanol reactants in which greater than 50 percent, more preferably greater than 60 percent and most preferably greater than 70 percent of the molecules are of linear (straight chain) carbon structure. In another embodiment, preference further exists for alkanol reactants in which greater than 50 percent, more preferably greater than 60 percent and most preferably greater than 70 percent of the molecules are of branched carbon structure.

The general suitability of such alkanols as reactants in alkoxylation reactions is well recognized in the art. Commercially available mixtures of primary mono-hydric alkanols prepared via the oligomerisation of ethylene and the hydroformylation or oxidation and hydrolysis of the resulting higher olefins are particularly preferred. Examples of commercially available alkanol mixtures include the NEODOL Alcohols,

trademark of and sold by Shell Chemical Company, including mixtures of C_9, C_{10} and C_{11} alkanols (NEODOL 91 Alcohol), mixtures of C_{12} and C_{13} alkanols (NEODOL 23 Alcohol), mixtures of C_{12}, C_{13}, C_{14} and C_{15} alkanols (NEODOL 25 Alcohol), and mixtures of C_{14} and C_{15} alkanols (NEODOL 45 Alcohol); the ALFOL Alcohols (ex. Vista Chemical Company), including mixtures of C_{10} and C_{12} alkanols (ALFOL 1012), mixtures of C_{12} and C_{14} alkanols (ALFOL 1214), mixtures of C_{16} and C_{18} alkanols (ALFOL 1618), and mixtures of C_{16}, C_{18} and C_{20} alkanols (ALFOL 1620), the EPAL Alcohols (Ethyl Chemical Company), including mixtures of C_{10} and C_{12} alkanols (EPAL 1012), mixtures of C_{12} and C_{14} alkanols (EPAL 1214), and mixtures of C_{14}, C_{16} and C_{18} alkanols (EPAL 1418), and the TERGITOL-L Alcohols (Union Carbide), including mixtures of C_{12}, C_{13}, C_{14} and C_{15} alkanols (TERGITOL-L 125). Also very suitable are the commercially available alkanols prepared by the reduction of naturally occurring fatty esters, for example, the CO and TA products of Proctor and Gamble Company and the TA alcohols of Ashland Oil Company.

Among the polyols, particular mention may be made of those having from 2 to 6 hydroxyl groups and 9 or more, preferably 9 to 30 carbon atoms. Specific examples include the alkylene glycols such as decylene glycol, the polyalkylene glycol ethers, such as tripropylene glycol and glycerine sorbitol. Higher oligomers and polymers of the polyols are also very suitable.

The active hydrogen containing reactant is also very suitably the alkoxylate product of a previous alkoxylation of an active hydrogen containing compound.

Further examples of both specific alkylene oxide reactants and specific active hydrogen containing reactants suitable for use in the present invention are recited in the aforementioned U.S. Patents.

For purposes of the present invention, the alkylene oxide reactant and the active hydrogen containing reactant are necessarily contacted in the presence of a catalyst comprising one or more of the phosphate salts of the rare earth elements of the present invention. The catalyst is applied in an amount which is effective to catalyse the alkoxylation reaction.

In terms of processing procedures, the alkoxylation reaction in the present invention may be conducted in a generally conventional manner. For example, the catalyst in the liquid active hydrogen containing reactant is contacted, preferably under agitation, with alkylene oxide reactant, which is typically introduced in gaseous form, at least for the lower alkylene oxides. Additional liquid active hydrogen containing reactant can optionally be added anytime before the addition of the alkylene oxide reactant. Thus, a concentrated catalyst reaction mixture can be made and a portion can be used as necessary.

In preferred embodiments, the alkylene oxide reactant is ethylene oxide or propylene oxide or a mixture of ethylene oxide and propylene oxide. In a further preferred embodiment, the active hydrogen containing reactant is an alcohol, a polyol or another hydroxyl containing compound. The reaction is carried out in the presence of a catalytically effective amount of the rare earth phosphate salt catalyst prepared according to the present invention. In a particularly preferred embodiment, ethylene oxide is contacted and

reacted with a C_9 to C_{30} primary alkanol in the presence of a catalytically effective amount of a catalyst for alkoxylation. Additional liquid active hydrogen containing reactant can be optionally added at any time in the process.

While these procedures describe a batch mode of operation, the present invention is equally applicable to a continuous process.

Overall, the two reactants are utilized in quantities which are predetermined to yield an alkoxylate product of the desired mean or average adduct number. The average adduct number of the product is not critical to this process. Such products commonly have an average adduct number in the range from less than one to 30, or greater.

In general terms, suitable and preferred process temperatures and pressures for purposes of the present invention are the same as in conventional alkoxylation reaction between the same reactants, employing conventional catalysts. A temperature of at least 90°C, particularly at least 120°C, and most particularly at least 130°C, is typically preferred from the standpoint of the rate of reaction, while a temperature less than 250°C, particularly less than 210°C, and most particularly less than 190°C, is typically desirable to minimize degradation of the product. As is known in the art, the process temperature can be optimized for given reactants, taking such factors into account.

Superatmospheric pressures, e.g. pressures between 68.9 and 1034.2 kPa g (10 and 150 psig), are preferred, with pressure being sufficient to maintain the active hydrogen containing reactant substantially in the liquid state.

When the active hydrogen containing reactant is a liquid and the alkylene oxide reactant is a vapour, alkoxylation is then suitably conducted by introducing alkylene oxide into a pressure reactor containing the liquid active hydrogen containing reactant and the catalyst. For considerations of process safety, the partial pressure of a lower alkylene oxide reactant is preferably limited, for instance, to less than 413.7 kPa a (60 psia), and/or the reactant is preferably diluted with an inert gas such as nitrogen, for instance, to a vapour phase concentration of about 50 percent or less. The reaction can, however, be safely accomplished at greater alkylene oxide concentration, greater total pressure and greater partial pressure of alkylene oxide if suitable precautions, known to the art, are taken to manage the risks of explosion. A total pressure of between 275.8 and 758.4 kPa g (40 and 110 psig), with an alkylene oxide partial pressure between 103.4 and 413.7 kPa g (15 and 60 psig), is particularly preferred, while a total pressure of between 344.7 and 620.5 kPa g (50 and 90 psig), with an alkylene oxide partial pressure between 137.9 and 344.7 kPa g (20 and 50 psig), is considered more preferred.

The time required to complete a process according to the present invention is dependent both upon the degree of alkoxylation that is desired (i.e. upon the average alkylene oxide adduct number of the product) as well as upon the rate of the alkoxylation reaction (which is, in turn, dependent upon temperature, catalyst quantity and nature of the reactants). A typical reaction time for preferred embodiments, particularly for when the alkylene oxide is gaseous, is less than 10 hours. When ethylene oxide is used as the alkylene oxide, the typical reaction

time is less than 2 hours. When propylene oxide is used as the alkylene oxide, the typical reaction time is less than 6 hours.

After the ethoxylation reaction has been completed, the product is preferably cooled. If desired, catalyst can be removed from the final product, although catalyst removal is not necessary to the process of the present invention. Catalyst residues may be removed, for example, by filtration, precipitation or extraction. A number of specific chemical and physical treatment methods have been found to facilitate removal of catalyst residues from a liquid product. Such treatments include contact of the alkoxylation product with strong acids such as phosphoric and/or oxalic acids or with solid organic acids such as NAFION H+ or AMBERLITE IR 120H; contact with alkali metal carbonates and bicarbonates; contact with zeolites such as type Y zeolite or mordenite; or contact with certain clays. Typically, such treatments are followed by filtration or precipitation of the solids from the product. In many cases filtration, precipitation or centrifugation is most efficient at elevated temperature.

Alkoxylation product mixtures prepared under the present invention are of high quality and have greater stability, relative to the product mixtures of acid or base catalysed alkoxylation reactions. The product mixtures prepared by the method of the present invention have viscosity of less than 50 Mpa.S (50 centipoise) and is fluid. The term "fluid" means having particles which easily move and change their relative position without a separation of the mass, and which readily yield to pressure.

In this regard, the present invention is particularly useful for the preparation of colourless or less coloured product relative to those of conventional practice, because the neutral salts do not promote degradation reactions which lead to colour forming impurities. Further, in a reaction mixture with propylene oxide, the reaction temperature is not limited to 125°C as opposed to using a typical basic catalyst such as KOH. In the process of the present invention, temperature as high as 180°C can be used without degradation of the product.

The following Examples are provided to further illustrate certain specific aspects of the present invention but are not intended to limit its broader scope.

COMPARATIVE EXAMPLE 1

A lanthanum phosphate compound was prepared by the following procedures. A first solution was prepared by dissolving 10 grams of $LaCl_3 \cdot 6H_2O$ in 200 grams of deionized water. A second solution was prepared by dissolving 10.64 grams of sodium orthophosphate ($Na_3PO_4 \cdot 12H_2O$) in 200 grams of water. The first solution (at room temperature) was added dropwise over a period of 25 minutes to the second solution (at 50°C). The resulting mixture was stirred for an additional 30 minutes at 50°C, and then filtered hot to separate a white precipitate. The filter cake was washed three times with 100 ml of 50°C deionized water. After drying, 7.4 grams of solid was recovered as a powder.

An alkoxylation process in accordance with the present invention was conducted under the following procedures. The alkylene oxide reactant for this process

embodiment consisted of ethylene oxide and the active hydrogen containing reactant consisted of NEODOL 23 Alcohol (NEODOL is a trademark) characterized as a mixture of primary, 80% linear (20% branched), alkanols having twelve and thirteen carbon atoms (about 40% by mol C_{12} and 60% by mol C_{13}).

Initially, 3.0 grams of the powder prepared as described above was added to 200 grams of NEODOL™ 23 Alcohol, and the mixture was heated to 130°C under nitrogen sparge for 3 hours to drive off water. The average particle size of the lanthanum phosphate compound was approximately 10 μm (10 micron). The resulting slurry was transferred to a one-litre autoclave reactor maintained under nitrogen atmosphere. The temperature of the reactor and contents was raised to 140°C. A mixture of nitrogen and ethylene oxide was then introduced into the reactor to a total pressure of 517.1 kPa a (75 psia) (310.3 kPa a nitrogen and 206.8 kPa a ethylene oxide (45 psia nitrogen and 30 psia ethylene oxide)). Alkoxylation (ethoxylation) commenced immediately. Additional ethylene oxide was supplied on demand to maintain an essentially constant 517.1 kPa (75 psia) pressure. Temperature was maintained at 140°C. A total of 315 grams of ethylene oxide was taken up over a period of 2.5 hours. The reactor was maintained for an additional hour to consume unreacted ethylene oxide in the system.

The product was waxy at room temperature and was analyzed by GC-LC techniques and found to have a mean average adduct number of 6.6. The only observed by-products were polyethylene glycols (PEG) in a quantity of 2.0% w.

Example 1

A fluid catalyst reaction mixture was prepared according to the following procedure. A total of 0.25 grams of lanthanum chloride hexahydrate (0.0007 moles) was added to 150 grams of NEODOL™ 23 alcohol (mixture of C_{12} and C_{13} having typical hydroxyl number of 289 mg/gKOH) from Shell Chemical Company (0.773 moles), and the reaction mixture was heated to 80°C. until a clear, colourless solution was produced. To this mixture was added dropwise 0.16 grams of a 42.5%w aqueous solution of phosphoric acid (0.0007 moles). The clear, colourless solution was heated to 120° C under a nitrogen sparge to remove water until a solution containing < 200 ppm H_2O was obtained. This mixture was transferred to the autoclave reactor system and ethoxylated at 165°C, according to the general procedures in the previous example. A total of 238 grams (5.41 moles) of ethylene oxide was added over a 90 minute period, producing an alkanol ethoxylate having a mean average adduct number of 7.0. The product mixture was a slightly hazy, colourless fluid product with a viscosity measured at 50 mPa.s (50cps). Viscosity was measured with a Brookfield viscosimeter.

Example 2

A fluid catalyst reaction mixture was prepared according to the procedure described in Example 1. A total of 2.19 grams (0.0038moles) of lanthanum octanoate obtained from Rhone-Poulenc was dissolved in 166 grams (0.814 moles) of NEODOL™ 25 alcohol (mixtures of C_{12}, C_{13}, C_{14} and C_{15} alkanols having a typical hydroxyl number of 276 mg/gKOH) from Shell Chemical Company at

100°C. To this mixture was added dropwise 0.45 grams of an 85%w solution of phosphoric acid (0.0038 moles). After drying the catalyst mixture at 120°C under N_2 sparge to a water content of <200 ppm, the reaction mixture was transferred to the autoclave system, and ethoxylated at 165°C. A total of 250 grams (5.7 moles) of ethylene oxide was added over a 120 minute period, producing an alkanol ethoxylate having a mean average adduct number of 7.0. The product mixture was a slightly hazy, colourless fluid product with a viscosity measured at 52 Mpa.s (52cps).

Example 3

A fluid catalyst reaction mixture was prepared according to the procedure described in Example 1. A total of 17.5 grams (0.0308moles) of lanthanum octanoate obtained from Rhone-Poulenc was dissolved in 400 grams (2.06 moles) of NEODOL™ 23 alcohol (mixture of C_{12} and C_{13} having typical hydroxyl number of 289 mg/gKOH) from Shell Chemical Company at 100°C. To this mixture was added dropwise 3.55 grams of an 85%w solution of phosphoric acid (0.0308 moles). After drying the catalyst mixture at 120°C under N_2 sparge to a water content of <200 ppm, the reaction mixture was transferred to a 3.79 L (1 gallon) autoclave system. The reaction mixture was heated to 160°C, and 725 grams (16.48 moles) of ethylene oxide was added over a 45 minute period. The reaction mixture was then reacted with 1195 grams (20.6 moles) of propylene oxide at 160°C over a 3 hour period. The reaction mixture was allowed to react for an additional 30 minutes to consume all oxide feed. The product mixture was an alkanol ethoxypropoxylate with a

mean average adduct number of 8.0 moles of EO and 10 moles of PO. Analysis of the reaction product by iodine number showed no measurable olefinic substrates. There was no allyl alcohol propoxylate formed.

Example 4:

A fluid catalyst reaction mixture was prepared according to the procedure described in Example 1. A total of 3.64 grams (0.0064moles) of lanthanum octanoate obtained from Rhone-Poulenc was dissolved in 500 mL of NEODOL™ 25 alcohol (mixtures of C_{12}, C_{13}, C_{14} and C_{15} alkanols having a typical hydroxyl number of 276 mg/gKOH) from Shell Chemical Company at 100°C. To this mixture was added dropwise 0.74 grams of an 85%w solution of phosphoric acid (0.0064 moles). After drying the catalyst mixture at 120°C under N_2 sparge to a water content of <200 ppm, the particle size was determined to have a median diameter of 0.7μm (0.7 microns) with standard deviation of 0.3μm (0.3 microns). Horiba Laser Scattering Particle Size Distribution Analyzer, LA-900 was used for the determination of particle size in the range of 0.05 to 1000μm (0.05 to 1000 microns).

C L A I M S

1. A process for the preparation of a fluid rare earth phosphate catalyst composition comprising:

a) providing a rare earth salt soluble in C_9-C_{30} active hydrogen containing organic compound at a temperature of less than 120°C;

b) adding and dissolving the rare earth salt in a C_9-C_{30} active hydrogen containing organic compound thereby producing a rare earth/organic solution; and

c) adding phosphoric acid to the rare earth/organic solution in a rare earth salt to phosphoric acid molar ratio in the range of 0.7:1 to 1.3:1 thereby producing the fluid rare earth phosphate catalyst composition.

2. The process of claim 1 wherein the molar ratio of rare earth salt to phosphoric acid is in the range of 0.9:1 to 1.1:1.

3. The process of claim 1 or 2 wherein the phosphoric acid is a phosphoric acid solution in a concentration in the range of 50 weight percent to 85 weight percent in water.

4. The process of claim 1, 2 or 3 wherein the rare earth salt comprises a lanthanum salt.

5. The process of any one of the preceding claims further comprising adding a base that does not contain a Group 1 or Group 2 of the elements of the periodic table in an amount effective to adjust the pH of the composition to a pH in the range of 5 to 8.

6. The process of any one of the preceding claims wherein the active hydrogen containing organic compound is a C_9-C_{30} primary mono-hydric alkanol or alkylphenol.

7. A process for the preparation of alkylene oxide adducts of active hydrogen containing organic compounds, which comprises contacting an alkylene oxide reactant comprising one or more vicinal alkylene oxides with an active hydrogen containing reactant comprising one or more active hydrogen containing organic compounds, in the presence of a catalytically effective amount of the fluid catalyst composition prepared by the process of any one of claims 1 to 6.

8. The process of claim 7 wherein the alkylene oxide reactant comprises one or more vicinal alkylene oxides and has 2 to 4 carbon atoms.

9. A process for the preparation of alkylene oxide adducts of primary monohydric alkanols, which comprises:

a) providing a rare earth salt soluble in C_9-C_{30} primary monohydric alkanols at a temperature of less than 120°C;

b) adding and dissolving the rare earth salt in a C_9-C_{30} primary monohydric alkanol solution thereby producing a rare earth/alkanol solution;

c) adding phosphoric acid to the rare earth/alkanol solution in a rare earth salt to phosphoric acid molar ratio in the range of 0.7:1 to 1.3:1 thereby producing the fluid rare earth phosphate catalyst in the alkanol;

d) optionally adding a base that does not contain a Group 1 or Group 2 of the elements of the periodic table in an amount effective to adjust the pH of the

catalyst in the alkanol to a pH in the range of 5 to 8; and

e) contacting an alkylene oxide reactant comprising one or more vicinal alkylene oxides and having 2 to 4 carbon atoms with the fluid rare earth phosphate catalyst in the alkanol, thereby producing the alkylene oxide adducts of primary monohydric alkanols.

10. A process for the preparation of alkylene oxide adducts of active hydrogen containing organic compounds, which comprises contacting an alkylene oxide reactant comprising one or more vicinal alkylene oxides with an active hydrogen containing reactant comprising one or more active hydrogen containing organic compounds, in the presence of a catalytically effective amount of the fluid rare earth phosphate catalyst prepared by the process comprising:

a) providing a rare earth salt soluble in the active hydrogen containing reactant at a temperature of less than 120°C;

b) adding and dissolving the rare earth salt in the active hydrogen containing reactant thereby producing a rare earth/organic solution; and

c) adding phosphoric acid to the rare earth/organic solution in a rare earth salt to phosphoric acid molar ratio in the range of 0.7:1 to 1.3:1 thereby producing the fluid rare earth phosphate catalyst.