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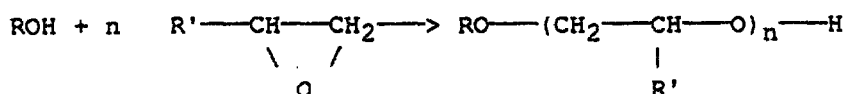
TS 0014

ALKOXYLATION PROCESS

The invention relates to an alkoxylation process for preparing alkyleneoxide adducts of active hydrogen-containing compounds.

Many of these alkyleneoxide adducts are of established commercial utility and, depending on their specific properties, may be employed, for example, in detergent compositions for use in industry and in the home, as solvents, lubricants, wetting or emulsifying agents or as intermediates for preparing polyurethane products.

The adducts are usually prepared by reacting one or more alkyleneoxide molecules with a molecule of an active hydrogen-containing compound in the presence of a suitable catalyst. An illustration of the conventional preparation of an alkyleneoxide adduct, by addition of a number of alkyleneoxide molecules to a single molecule of an active hydrogen-containing compound, in casu an alcohol, is presented by the following equation:



In this equation R represents an alkylgroup, R' represents a hydrogen atom or an alkylgroup and n indicates the adduct number.

A problem, encountered in many prior art processes of this type, consists in the relatively low production of the envisaged alkyleneoxide adducts, due to insufficient activity of the selected catalyst. In particular in the preparation of adducts of the above formula, wherein R' represents an alkylgroup, it has been observed that usually adducts are produced having relatively low adduct numbers "n" e.g. below 10. Also, time-yield values are often unsatisfactory as a result of the required induction period, before the reaction initiates.

Moreover, with most of the catalysts used in the known alkoxylation processes, side reactions occur which result in the

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formation of undesirable products, e.g. unsaturated compounds, formed by dehydration of intermediately formed allyl compounds.

Alkylenoxide addition reactions are known to produce mixtures of various alkoxylate molecules having different numbers of oxyalkylene units, i.e. having different adduct numbers "n". The adduct number is a factor which in many respects controls the properties of the alkoxylate molecules and it is therefore desirable, for each intended use, to produce a mixture of alkoxylate molecules having adduct numbers within a relatively narrow range. It has been observed that with many catalysts, used in prior art processes, in particular with alkaline catalysts such as potassiumhydroxide, a broad range of alkylenoxide adducts is produced.

Accordingly, much effort has been made to find more active and more selective catalysts which can be used to produce at adequate rate, an alkylenoxide adduct mixture in which a relatively large proportion of the alkoxylate molecules have an adduct number "n" within a relatively narrow range.

In US Patent Specification 4,967,016 a process for the preparation of alkylenoxide adducts of active hydrogen-containing organic compounds is disclosed whereby a catalyst is used comprising a catalytically effective amount of bariumphosphate. The preparation of this catalyst is performed by neutralization of bariumhydroxide or bariumoxide with phosphoric acid in an aqueous medium. Typically, diluted phosphoric acid is added to an aqueous solution of bariumhydroxide. The formed suspension is filtered and the resulting solid (crystalline $\text{Ba}_3(\text{PO}_4)_2$) is washed with water and dried. Subsequently, the dried bariumphosphate is used as catalyst in an alkoxylation process, exemplified by ethyleneoxide as alkylenoxide.

It has now been found that the use of a bariumphosphate catalyst which has been activated before use, results in a significant increase in reaction rate and a reduction in induction period.

The present invention relates to a process for the preparation of alkylenoxide adducts of active hydrogen-containing organic



compounds by reaction of a compound having a vicinal oxide group with a compound containing at least one active hydrogen atom, in the presence of a catalyst obtainable by an activation treatment comprising treating with an alkali hydroxide solution.

5 Suitable compounds having a vicinal oxide (epoxide) group include vicinal alkyleneoxides, in particular the lower alkyleneoxides with 2 to 4 carbon atoms per molecule. Preferably, the epoxide group is at a terminal position such as in ethyleneoxide or propyleneoxide, but non-terminal alkyleneoxides, such as 2,3-
10 epoxybutane are not excluded.

 In the process of the invention, a preferred vicinal alkyleneoxide is propyleneoxide which can be converted in good yield into various polyether polyols having molecular weights within selected narrow ranges.

15 If desired, mixtures of alkyleneoxides may be used, for example a mixture of propyleneoxide and ethyleneoxide.

 Suitable compounds containing at least one active hydrogen atom include alcohols, thiols, phenols, carboxylic acids, amines of sufficient acidity and water.

20 Preference generally exists for hydroxyl-containing reactants, in particular monohydric or polyhydric alcohols. They may contain linear or branched carbon chains in their molecules, which chains may be interrupted by one or more hetero-atoms such as oxygen atoms.

 Examples of suitable active hydrogen-containing compounds are
25 lower alcohols such as propanol, butanol and hexanol, higher alcohols such as octanol, decanol, or mixtures of alcohols having from 8 to 20 carbon atoms such as mixtures of C₉, C₁₀ and C₁₁ alcohols, or mixtures of C₁₂, C₁₃, C₁₄ and C₁₅ alcohols, dihydric alcohols such as alkylene glycols, e.g. ethylene glycol, propylene
30 glycol, hexylene glycol, polyols such as glycerol and pentaerythritol, polyalkylene glycolethers such as diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol and polypropylene glycol, phenols such as phenol, p-methylphenol, octylphenol and decylphenol, diphenols such
35 as resorcinol and diphenylol propane, alkanethiols such as 2-



propanethiol, 2-butanethiol and 3-pentanethiol, mono- and dicarboxylic acids such as acetic acid, propionic acid, valeric acid, lauric acid, palmitic acid, caproic acid, steric acid, oleic acid, benzoic acid, toluic acid, terephthalic acid and maleic acid, tertiary alkylamines and hydroxyl-containing amines such as N,N-diethylethanolamine and tripropanolamine.

Preferably, a di- or polyhydric alcohol or a glycolether is used, in particular glycerol or polypropylene glycol. These compounds have proved to be in particular suitable for preparing alkyleneoxide adducts of which the adduct numbers are within a selected, relatively narrow range. Thus, dihydric and polyhydric alcohols and glycolethers have been advantageously used for preparing alkyleneoxide adducts having adduct numbers in the range of 20 to 40, or alkyleneoxide adducts having adduct numbers in the range of 80 to 100.

The process according to the present invention is of particular interest for preparing polyols by reacting propyleneoxide with a polypropylene glycol. The resulting propyleneoxide adducts are eminently suitable as starting materials for the production of polyurethanes.

According to the invention, the process is carried out with a catalyst comprising bariumphosphate obtainable by an activation treatment comprising treating with an alkali hydroxide solution. If desired the catalyst may comprise in addition other materials, for example catalyst promoters or other catalytically active or substantially inert materials such as non-activated bariumphosphate or minor amounts of other barium compounds. However, it is preferred to use a catalyst essentially consisting of activated bariumphosphate. The amount of bariumphosphate present in the catalyst is preferably more than 80% by weight, based on total amount of catalyst, more preferably more than 85% by weight, more preferably more than 95% by weight. The amount of catalyst is not critical, but is usually selected such that the supplied quantity of activated bariumphosphate is in the range of 0.1 to 2% by weight, based on the amount of eventually produced alkyleneoxide adduct.



An attractive procedure consists in effecting the activation treatment directly after formation of bariumphosphate occurs, i.e. before isolating bariumphosphate from the aqueous mixture in which it was formed.

5 In this embodiment the activation treatment preferably includes a step whereby bariumphosphate, directly after its formation, is contacted with an aqueous solution of an alkalihydroxide.

Suitable alkalihydroxides include the hydroxides of sodium, potassium, rubidium and cesium. Of these, sodiumhydroxide is in particular preferred.

10 The amount of alkalihydroxide solution added to the bariumphosphate-containing mixture may vary, but is preferably selected such that activated bariumphosphate is obtained as a precipitate in an essentially neutral medium. Hence, it is preferred to add an excess of phosphoric acid in the preparation of bariumphosphate, in order to obtain an essentially neutral medium containing activated bariumphosphate.

The activated bariumphosphate may be recovered by filtration followed by washing, e.g. with water, and drying, suitably at elevated temperature.

20 Preferably, the activated bariumphosphate, after washing with water, is subjected to a treatment with an organic solvent, before drying, in order to remove a substantial amount of washing liquid.

Suitable organic solvents for this purpose include aprotic polar solvents such as ethers, for example diethylether or tetrahydrofuran. Tetrahydrofuran is in particular preferred.

25 If desired, the activation treatment may also be effected after isolation of bariumphosphate from the reaction medium in which it has been prepared. In this mode of operation the amount of phosphoric acid, added during the preparation of bariumphosphate, advantageously corresponds to the stoichiometric amount required for obtaining an essentially neutral reaction medium.

30 After subjecting the isolated bariumphosphate to an activation treatment, such as a treatment with an aqueous solution of an alkalihydroxide, conveniently a washing and a drying step is



effected, suitably in the manner as described above.

The activated bariumphosphate can be used as catalyst, both in batchwise and in continuous operation of the alkoxylation process. The invention is further illustrated by the following examples.

5 Example 1

A 3-litre roundbottom reactor was charged with 2000 ml of water. Subsequently 0.9 mol of bariumhydroxide monohydrate ($\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$) was added and the temperature of the mixture was raised to 50 °C.

10 The mixture was filtered through a glass-filter and the temperature of the filtrate was again raised to 50 °C. During a period of 16 minutes under stirring, 0.66 mol of phosphoric acid (85% wt in water) was added. Subsequently, 0.352 mol of sodiumhydroxide in 30 ml of water was added and the mixture was
15 stirred (200 rpm) during 2 hours.

The resulting mixture was split in three parts, each part being filtered through a glass-filter, washed with water (3 times, each time with 200 ml of water), washed with tetrahydrofuran (3 times, each time with 200 ml of tetrahydrofuran) and dried overnight at
20 100 °C under vacuum.

The activity of the obtained bariumphosphate catalyst for the preparation of polyetherpolyols was investigated in a 1 litre steel autoclave, fitted with a magnetic impeller stirrer and equipped with safety devices for high temperature and pressure conditions.

25 The autoclave was charged with 51.5 g of polypropylene glycol having a molecular weight of 400 g/mol (PPG 400) and 4 g of bariumphosphate catalyst, prepared as described above.

The autoclave was sealed and, after raising the temperature of its contents to 120 °C, evacuated during 30 minutes. After addition
30 of nitrogen (1 bar), 748 g of propyleneoxide was pumped into the autoclave under pressure regulation (6 bar abs.) to yield a product with a targeted molecular weight of 6000 g/mol.

Subsequently the reaction was allowed to react down without further pressure regulation. The propoxylation time was
35 approximately 100 minutes, the total batch time was 6 hours.



With propoxylation time is meant the time span between adding propylene oxide and obtaining the targeted product for the first time.

5 The volatiles were removed from the mixture at 120 °C under vacuum.

The product was worked-up by stirring the mixture with alkaline water, followed by filtration, neutralization and another filtration. The obtained polyether polyol was clear and had an unsaturation value below 20 mmol/kg.

10 Example 2

A 3-litre reactor was charged with 1500 ml of water of 25 °C, containing 79.2 mmol of bariumhydroxide monohydrate. To this solution 52.8 mmol of phosphoric acid in 100 ml of water was added during 8 minutes.

15 For 2 hours the mixture was stirred at 25 °C and then filtered. After washing with 600 ml of water the mixture was filtered again and dried during 24 hours at 120 °C, yielding pure bariumphosphate.

For the activation of bariumphosphate, obtained as described above, a quantity of 65 g (108 mmol) of bariumphosphate was added at
20 a temperature of 50 °C to a solution of 6.5 g of potassiumhydroxide (116 mmol) in 650 ml of water. The mixture was stirred at 50 °C during 2 hours. The mixture was filtered using a glass-filter and the filtrate was washed with water (3 times, each time with 200 ml of water), washed with tetrahydrofuran (3 times, each time with
25 200 ml of tetrahydrofuran) and dried in an oven under vacuum during 24 hours at 100 °C.

The activated pure bariumphosphate thus obtained, was used as catalyst for the preparation of polyether polyols, substantially as described in Example 1. The supply of propyleneoxide was adapted to
30 yield a product with a targeted molecular weight of 3000 g/mol. The propoxylation time again was approximately 100 minutes, the total batch time was 3 hours.

Example A (for comparison, not according to the invention)

Bariumphosphate was prepared, substantially as described in
35 Example 2. However, no activation treatment was carried out. The



obtained bariumphosphate was directly used as catalyst in the propoxylation process, substantially as described in Example 1, but carried out at a temperature of 150 °C. The propoxylation time was approximately 250 minutes. The propoxylation time contained an induction period of about 175 minutes. The total batch time was 8.9 hours.

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C L A I M S

1. A process for the preparation of alkyleneoxide adducts of active hydrogen-containing organic compounds by reaction of a compound having a vicinal oxide group with a compound containing at least one active hydrogen atom, in the presence of a catalyst comprising bariumphosphate obtainable by an activation treatment comprising treating with an alkali hydroxide solution.
2. A process as claimed in claim 1, characterized in that the compound having a vicinal oxide group is an alkyleneoxide with 2 to 4 carbon atoms.
3. A process as claimed in claim 1 or 2, characterized in that the compound containing at least one active hydrogen atom is a di- or polyhydric alcohol or a glycolether.
4. A process as claimed in any of claims 1-3, characterized in that alkyleneoxide adducts are prepared having an adduct number in the range of 20 to 40.
5. A process as claimed in any of claims 1-4, characterized in that the activation treatment is performed during the preparation of the catalyst.
6. A process as claimed in claim 5, characterized in that the activation treatment includes contacting bariumphosphate, with an aqueous solution of an alkali hydroxide directly after its formation.
7. A process as claimed in claim 6, characterized in that an aqueous solution of sodium hydroxide is used.
8. A process as claimed in claim 6 or 7, characterized in that the amount of alkali hydroxide in the aqueous alkali hydroxide solution is selected such that activated bariumphosphate is obtained as a precipitate in an essentially neutral medium.
9. A process as claimed in any of claims 5-8, characterized in that the activated catalyst, before use, is washed with water, followed by a treatment with an organic solvent and dried.
10. A process as claimed in any one of claims 1-9, characterized in





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that propyleneoxide is reacted with a polypropylene glycol.

11. Alkyleneoxide adducts whenever obtained by a process as claimed in any of claims 1-10.

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