

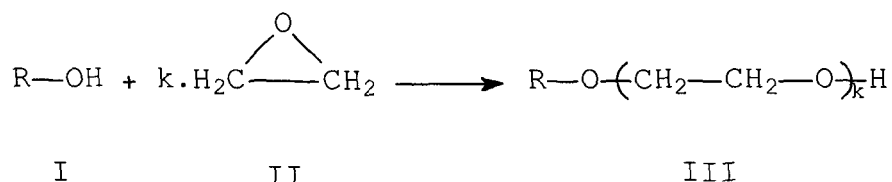
PROCESS FOR PREPARING AN ALKOXYLATED ALCOHOL OR PHENOL

The present invention relates to a process for preparing an alkoxyated alcohol or phenol.

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 either being 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.

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



The term "alkoxylate", as used herein, refers to any product of the addition reaction of a number (k) of alkylene oxide molecules to a single active hydrogen containing organic compound.

5 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 k in formula III above. The adduct
10 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.

15 In the preparation of alkoxylated alcohols it is often the case that primary alcohols are more reactive, and in some cases substantially more reactive than the corresponding secondary and tertiary compounds. For example, this means that it is not always possible to
20 directly ethoxylate secondary and tertiary alcohols successfully since the reactions with the starting alcohol can be slow and can lead to a high proportion of unreacted secondary and tertiary alcohols, respectively, and the formation of secondary alcohol ethoxylates and
25 tertiary alcohol ethoxylates, respectively, with a very wide ethylene oxide distribution.

 Secondary alcohols can be derived from relatively cheap feedstocks such as paraffins (by oxidation), such as those paraffins produced from Fischer-Tropsch
30 technologies, or from short chain C₆-C₁₀ primary alcohols (by propoxylation). For this reason it would be desirable to develop a suitable process for the direct alkoxylation of secondary alcohols. It has surprisingly

been found by the present inventors that secondary and tertiary alcohols, as well as primary alcohols, may be successfully alkoxylation by carrying out the alkoxylation reaction in the presence of hydrogen fluoride and a boron-containing compound.

The alkoxylation products can contain reduced levels of free unreacted alcohol and have a narrow range of alkylene oxide adduct distribution, compared to the adducts prepared with an alkali metal hydroxide catalyst. Their process of production is usually easier and more flexible than that with a double metal cyanide DMC catalyst, as the reaction temperature can be varied over a wide range e.g. -20 to 150°C and the catalyst is simpler to use than the DMC one which requires a complex catalyst synthesis. The process of the invention can also give a much higher yield of alkoxylation product compared to use as catalyst of alkali metal hydroxide or hydrogen fluoride in the absence of boron containing compound with at least one B-O bond.

US-A-4456697 describes the alkoxylation of many types of compound, among which are primary and secondary alcohols, in the presence of hydrogen fluoride and a metal alkoxide; use only of primary alcohols is exemplified.

US-A-5034423 describes the production of polyether polyols from an epoxy compound in the presence of a reactive hydroxyl containing compound, boric acid, an epoxy catalyst such as boron trifluoride, and a basic salt.

WO 03/044074 describes the production of polyether polyols from an alkylene oxide in the presence of an initiator, which may be a hydroxyl compound with at least one hydroxy group, but is preferably a polyol such as

glycerol, the reaction being catalysed by hydrogen fluoride and a double metal cyanide catalyst and optionally in the presence of a cocatalyst which may be among many others boric acid or trimethyl borate. In Ex
5 2 glycerol is reacted with propylene oxide in the presence of hydrogen fluoride and trimethyl borate, followed by stripping and further reaction with propylene oxide in the presence of a double metal cyanide catalyst to produce a polyether polyol of weight-average molecular
10 weight of 3000g/mol.

Co-pending PCT application PCT/EP04/051366 published after the priority date of the present application as WO 2005/005360 discloses in Comparative Example D the preparation of an C₁₄/C₁₅ primary alcohol ethoxylate by
15 ethoxylating a C₁₄/C₁₅ primary alcohol composition in the presence of HF and trimethyl borate. There are no examples in this application of the alkoxylation of secondary or tertiary alcohols.

Summary of the Invention

20 According to the present invention there is provided a process for preparing an alkoxyated alcohol comprising reacting a starting mono-hydroxy alcohol selected from secondary alcohols, tertiary alcohols and mixtures thereof, with an alkylene oxide in the presence of
25 hydrogen fluoride and a boron-containing compound comprising at least one B-O bond.

According to another aspect of the present invention there is provided the use of hydrogen fluoride and a boron-containing compound comprising at least one B-O
30 bond for the alkoxylation of secondary and tertiary mono-hydroxy alcohols.

According to a further aspect of the present invention there is provided a process for preparing an alkoxyated primary alcohol comprising reacting a primary mono-hydroxy alcohol with an alkylene oxide in the presence of hydrogen fluoride and a boron-containing compound comprising at least one B-O bond wherein is excluded a process which comprises reacting a C14/C15 primary alcohol with ethylene oxide in the presence of HF and trimethyl borate.

According to a further aspect of the present invention there is provided a process which comprises reacting a primary mono-hydroxy alcohol with an alkylene oxide in the presence of hydrogen fluoride and a boron-containing compound comprising at least one B-O bond, wherein the boron-containing compound is selected from boric acid and boric acid anhydrides.

Detailed Description of the Invention

The process according to one aspect of the present invention comprises reacting a starting mono-hydroxy alcohol selected from secondary alcohols, tertiary alcohols and mixtures thereof with an alkylene oxide in the presence of hydrogen fluoride and a boron-containing compound comprising at least one B-O bond.

While the process of the present invention gives particular advantages versus conventional processes for the alkoxylation of secondary and tertiary alcohols in terms of providing a way to directly ethoxylate secondary and tertiary alcohols to give ethoxylated alcohol products having low levels of unreacted, residual alcohol and a narrow ethoxylate distribution, the process of the present invention is also suitable for the alkoxylation of primary mono-hydroxy alcohols.

Suitable starting alcohols for use in the preparation of alkoxyated alcohols herein include alkanols, such as ones of 1 to 30 carbon atoms.

5 Preference can also be expressed, for reasons of both process performance and commercial value of the product, for alcohols in particular alkanols having from 6 to 30 such as 9 to 30 carbon atoms, with C₉ to C₂₄ alcohols considered more preferred and C₉ to C₂₀ alcohols considered most preferred, including mixtures thereof,
10 such as a mixture of C₉ and C₂₀ alcohols. As a general rule, the alcohols may be of branched or straight chain structure depending on the intended use. In one embodiment, preference further exists for alcohol reactants in which greater than 50 percent, more
15 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 alcohol reactants in which greater than 50 percent, more
20 preferably greater than 60 percent and most preferably greater than 70 percent of the molecules are of branched carbon structure.

The secondary starting alcohol is preferably an alkanol with one hydroxyl group, especially situated in a
25 2, 3, 4, 5 or 6 carbon atom, numbering from the end of the longest carbon chain. The alkanol is preferably linear. Examples of secondary alcohols suitable for use herein include 2-undecanol, 2-hexanol, 3-hexanol, 2-heptanol, 3-heptanol, 2-octanol, 3-octanol, 2-nonanol, 2-
30 decanol, 4-decanol, 2-dodecanol, 2-tetradecanol, 2-hexadecanol and mixtures thereof, especially of alkanols

of the same carbon content. 2,6,8-trimethyl-4-nonanol may be used.

The tertiary alcohol starting alcohol is preferably an alkanol of 4-24 especially 9-20 carbon atoms, and may
5 be of formula IV, $R^1(R^2)C(R^3)OH$, wherein each of R^1 R^2 and R^3 , which are the same or different, represents an alkyl group of 1-20 carbons. R^1 preferably represents alkyl of 4-18 carbons, which may be linear or have at least one methyl or ethyl branch while R^2 and R^3
10 preferably represent alkyl of 1-8 carbons e.g. methyl, ethyl, propyl, isopropyl isobutyl, butyl or hexyl; . Examples of tertiary alcohols suitable for use herein include hydroxylated mainly terminally (mainly 2- and 3-) methyl-branched C_9 - C_{20} paraffins emerging from a Fischer-
15 Tropsch process.

Commercially available mixtures of primary monohydric alkanols prepared via the oligomerisation of ethylene and the hydroformylation or oxidation and hydrolysis of the resulting higher olefins are also
20 suitable as starting alcohols in the process herein. Examples of commercially available primary 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} ,
25 C_{13} , C_{14} and C_{15} alkanols (NEODOL 25 Alcohol), and mixtures of C_{14} and C_{15} alkanols (NEODOL 45 Alcohol, and NEODOL 45E Alcohol); the ALFOL Alcohols (ex. Vista Chemical Company), including mixtures of C_{10} and C_{12}
30 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 C₁₆, C₁₈ and C₂₀ alkanols (ALFOL 1620), the EPAL Alcohols (Ethyl Chemical Company), including mixtures of C₁₀ and C₁₂ alkanols (EPAL 1012), mixtures of C₁₂ and C₁₄ alkanols (EPAL 1214), and
5 mixtures of C₁₄, C₁₆ and C₁₈ alkanols (EPAL 1418), and the TERGITOL-L Alcohols (Union Carbide), including mixtures of C₁₂, C₁₃, C₁₄ and C₁₅ alkanols (TERGITOL-L 125). Also suitable for use herein is NEODOL 1, which is primarily a C₁₁ alkanol. Also very suitable are the
10 commercially available alkanols prepared by the reduction of naturally occurring fatty esters, for example, the CO and TA products of Procter and Gamble Company and the TA alcohols of Ashland Oil Company.

Especially preferred starting alcohols for use in
15 the process of the present invention are secondary alcohols.

Mixtures of primary and/or secondary and/or tertiary alcohols are also suitable for use herein. For example, mixtures of primary and secondary and tertiary alcohols
20 can be used herein. As another example, mixtures of primary and tertiary alcohols can be used herein.

Mixtures of alcohols comprising primary and secondary alcohols are particularly suitable for use herein.

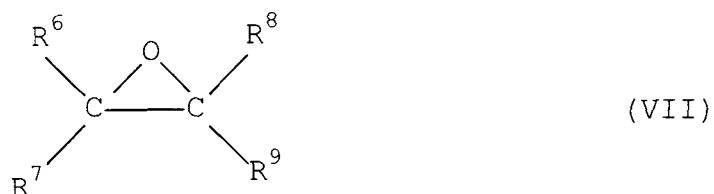
25 Mixture of alcohols comprising secondary and tertiary alcohols are also particularly suitable for use herein.

In particular, oxidation products arising from Fischer-Tropsch derived paraffins (which may include
30 mixtures of primary and secondary alcohols) are particularly suitable for use herein.

A phenol may also be alkoxyated in the same way as described herein for the alkoxylation of the starting alcohol. In an alternative process of the present invention, there is provided process for preparing an alkoxyated phenol comprising reacting a starting mono-
5 hydroxy phenol with an alkylene oxide in the presence of hydrogen fluoride and a boron-containing compound comprising at least one B-O bond.

The mono-hydroxy phenol may have 1-3 aromatic rings, optionally substituted with at least one inert, non hydroxylic substituent such as alkyl. The phenol may be phenol, α or β -naphthol or be based on a phenol ring, or on a naphthol ring, either with at least 1 e.g. 1-3 alkyl substituents, each of 1-20 carbon atoms, preferably 1-3
15 such as methyl or ethyl, or 6-20 carbons such as hexyl, octyl, nonyl, decyl, dodecyl or tetradecyl. The alkyl group(s) may be linear or branched. The substituted phenol may be p-cresol or a nonylphenol, especially a linear or branched one or one which is a mixture of
20 branched nonylphenols, optionally with n-nonyl phenol.

Suitable alkylene oxide reactants for use herein include an alkylene oxide (epoxide) reactant which comprises one or more vicinal alkylene oxides, particularly the lower alkylene oxides and more
25 particularly those in the C₂ to C₄ range. In general, the alkylene oxides are represented by the formula (VII)



wherein each of the R⁶, R⁷, R⁸ and R⁹ moieties is preferably individually selected from the group

consisting of hydrogen and alkyl moieties but may be individually selected from the group consisting of hydrogen, alkyl and hydroxyalkyl moieties with the proviso that in the formula VII there are no more than 2 hydroxyalkyl groups e.g. one but preferably none.

Reactants which comprise ethylene oxide, propylene oxide, butylene oxide, glycidol, or mixtures thereof 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.

For preparation of the alkoxyate compositions herein the alkylene oxide reactant and the starting alcohol are contacted in the presence of hydrogen fluoride and a boron-containing compound.

The hydrogen fluoride can be added as such or can be formed in-situ. Hydrogen fluoride can be formed in-situ for example by the use of compounds from which hydrogen fluoride can be separated off at reaction conditions. Hydrogen fluoride can be obtained by acidification with mineral acid e.g. sulphuric acid or alkaline earth metal fluorides e.g. calcium, strontium or barium difluoride. The HF may be generated in situ by adding to the reaction mixture a reactive fluorine containing compound that forms HF in that mixture such as a mixed anhydride of HF and an organic or inorganic acid. Examples of such compounds are acyl fluorides such as alkanoyl fluorides e.g. acetyl fluoride or aryl carbonyl fluorides e.g. benzoyl fluoride, or organic sulphonyl fluorides such as

trifluoromethyl sulphonyl fluoride, or sulphuryl or thionyl fluoride. Preferably, the hydrogen fluoride is added as such to the process of the present invention; the hydrogen fluoride may be added as aqueous HF e.g. of 30-50 % by wt concentration but is preferably anhydrous.

The hydrogen fluoride is present in such an amount that it catalyses the reaction of the starting alcohol with the one or more alkylene oxides. The amount needed to catalyse the reaction depends on the further reaction circumstances such as the starting alcohol used, the alkylene oxide present, the reaction temperature, further compounds which are present and which may react as co-catalyst, and the desired product. Generally, the hydrogen fluoride will be present in an amount of from 0.0005 to 10%, by weight, more preferably of from 0.001 to 5%, by weight, more preferably of from 0.002 to 1 %, by weight especially 0.05 to 0.5 % by weight, based on the total amount of starting alcohol and alkylene oxide.

The presence of a boron-containing compound comprising at least one B-O bond in combination with hydrogen fluoride has been found to be particularly useful for catalyzing the reaction of an alcohol with an alkylene oxide.

Suitable boron-containing compounds comprising at least one B-O bond for use herein include boric acid (H₃BO₃), boric acid anhydrides, alkyl borates, and mixtures thereof. Suitable compounds may contain 1-3 B-O bonds in particular 3 B-O bonds, as in boric acid or trimethyl borate.

The boron-containing compounds for use herein can either be introduced into the process as such or formed from their organoborane precursor(s) by hydrolysis or alcoholysis in-situ.

Examples of suitable boric acid anhydrides for use herein include meta boric acid (HBO_2), tetra boric acid ($\text{H}_2\text{B}_4\text{O}_7$) and boron oxide (B_2O_3).

5 Examples of suitable alkyl borates for use herein include trimethyl borate, triethyl borate, tripropyl borate, tri-isopropyl borate, tributyl borate and the boric ester derived from the starting (secondary) alcohol or its ethoxylate; trimethyl borate is preferred.

10 It is possible to prepare boron compounds having at least one B-O bond in-situ. For example the compound 9-borabicyclo[3.3.1]nonane (BBN) which does not contain any B-O bonds can be used to prepare 9-methoxy and/or 9-hydroxy BBN on contact with methanol or water in the reaction mixture.

15 Preferred boron-containing compounds for use herein are selected from boric acid, boric acid anhydrides and mixtures thereof.

A particularly preferred boron-containing compound for use in the present process, especially from the
20 viewpoint of providing an alkoxyated alcohol with relatively low levels of residual alcohol and a relatively narrow alkoxyate distribution is boric acid.

The boron containing compound comprising at least one B-O bond is present in such an amount that it acts as
25 co-catalyst for the reaction of the starting alcohol with the one or more alkylene oxides. The amount needed depends on the further reaction circumstances such as the starting alcohol used, the alkylene oxide present, the reaction temperature, further compounds which are present and which may react as co-catalyst, and the desired
30 product. Generally, the boron containing compound comprising at least one B-O bond will be present in an amount of from 0.0005 to 10%, by weight, more preferably

of from 0.001 to 5%, by weight, more preferably of from 0.002 to 1 %, by weight, especially 0.05 to 0.5 % by weight based on the total amount of starting alcohol and alkylene oxide.

5 The weight ratio of said boron containing compound to hydrogen fluoride is usually 100:1 to 1:100, preferably 1:10 to 10:1, especially 3:1 to 1:3.

 The alkoxylation process may be performed at -20°C to 200°C, such as 0-200°C, but preferably 50-130°C or
10 especially at less than 70°C or 50°C such as 0-50°C, in particular to reduce byproduct formation.

 In preferred alkoxyated alcohols produced by the process of the present invention, the amount of free alcohol is no more than 3%, more preferably no more than
15 1%, even more preferably no more than 0.5% by weight of the alkoxyated alcohol.

 At the end of the reaction, when the desired number of alkylene oxide units has been added to the alcohol, the reaction may be stopped by removal of the HF and/or
20 the alkylene oxide. The acid may be removed by adsorption, by ion exchange with a basic anion exchange resin, or by reaction such as by neutralization. The alkylene oxide may be removed by evaporation, in particular under reduced pressure and especially at less
25 than 100 °C, such as 40-80 °C.

 Examples of suitable ion exchange resins are weakly or strongly basic or anion exchange resins to remove the fluorine anion; they may be at least in part in their chloride or hydroxyl form. Examples of these resins are
30 those sold under the Trade Mark AMBERJET 4200 and AMBERLITE IRA 400. The reaction product may be mixed with the ion exchange resin in a batch operation and

subsequently separated therefrom but preferably the removal is in a continuous operation with the resin in a column through which is passed the reaction product.

Another method of inactivating the HF is by
5 neutralization. This may be performed with a base or with a salt of a strong base and weak acid. The base or salt may be inorganic, in particular one with at least some solubility in the reaction product such as at least 10g/l. The neutralization agent may be an alkali metal or
10 ammonium carbonate or bicarbonate such as sodium carbonate or ammonium carbonate or the corresponding hydroxide such as sodium hydroxide; ammonia gas may be used. Preferably the neutralization agent is an organic compound such as an organic amine with at least one
15 aminic nitrogen atom such as 1-3 such atoms. Examples of suitable amines are primary secondary or tertiary mono or diamines. The organic group or groups attached to the amine nitrogen[s] may be an optionally substituted alkyl group of 1-10 carbons such as methyl ethyl, butyl, hexyls
20 or octyl, or hydroxyl substituted derivative thereof such as hydroxyethyl, hydroxypropyl, or hydroxyisopropyl, or an aromatic group such as a phenyl group optionally substituted by at least one alkyl substituent e.g. of 1-6 carbon atoms such as methyl or inert substituent such as
25 halogen e.g. chlorine. Heterocyclic nitrogenous bases may also be used in which the ring contains one or more nitrogen atoms, as in pyridine or an alkyl pyridine. Preferably the organic neutralization agent is a hydroxyalkyl amine, especially a mono amine, with 1, 2 or
30 3 hydroxyalkyl groups, the other valency(ies) if any on the nitrogen being met by hydrogen or alkyl; the hydroxyalkyl and alkyl groups contain 1-6 carbons such as in 2 hydroxyethyl groups. Oligoalkyleneglycolamines

may also be used. The preferred amines are diethanolamine, triethanolamine and the corresponding isopropanolamines. The basic compound may be added in amount to neutralize at least half of the HF and preferably at least all of it.

Another type of agent to inactivate the HF is a reagent capable with the HF of forming a volatile fluoride. Silicon dioxide is an example of such a reagent as this forms silicon tetrafluoride which can be volatilised away from the alkoxyated product in a subsequent stripping stage.

The removal or inactivation of the HF is usually performed at a temperature below 100°C such as 20-80°C or especially while keeping the temperature below 40°C.

The removal or inactivation of the HF can be performed before or after any removal or stripping to reduce the content of volatiles such as unreacted alkylene oxide, any by-products such as 1,4-dioxane and possibly unreacted alcohol feedstock. The removal is preferably performed under reduced pressure and may be at a temperature below 150 °C, preferably below 100 °C such as 40-70 °C; advantageously the removal of volatiles is aided with passage of inert gas such as nitrogen through the reaction product. When the removal of the HF occurs before the stripping, any base used to neutralize the HF is preferably inorganic or maybe of much higher volatility [e.g. with an atmospheric boiling point below 100 °C or an amine containing less than 6 carbon atoms] than when the stripping occurs before the removal of HF. In the latter case any base is preferably inorganic or of low volatility [e.g. with an atmospheric boiling point above 150 °C or an amine containing more than 12 carbon

atoms]. By this means in the former case, the stripping will help to remove traces of residual volatile base. Preferably the stripping is performed before removal of the HF by addition of an amine of low volatility as described above or a non volatile amine.

After the stripping and the removal of the HF the alkoxyated product may be ready for used as such, for example in detergents, or may be further purified eg to separate unreacted alcohol, fluoride salts and/or improve its colour before use.

The invention will be further illustrated by the following examples, however, without limiting the invention to these specific embodiments.

Examples

Example 1 - Ethoxylation of the secondary alcohol 2-undecanol

To a "Teflon" bottle, equipped with a magnetic stirring bar and immersed in a (water) cooling bath, was charged with 2-undecanol (58 mmol, 10g), boric acid (50mg) and hydrogen fluoride (50mg). Ethylene oxide was added in the gas-phase at atmospheric pressure, at such a rate that the temperature did not exceed 50°C. After about 3 hours, 15.8 g of ethylene oxide (358 mmol) was consumed which corresponds with a degree of ethoxylation of 6.2 on intake) and then the product was treated with ca. 50mg of diethanol amine. The yield of ethoxylated 2-undecanol was 0.316 kg EO/per g HF.

Measurement of the average number of moles of ethylene oxide per mole of 2-undecanol, the ethoxylate distribution and residual free alcohol was performed using high performance liquid chromatography (HPLC). The technique for these measurements involved derivatising

the ethoxylated alcohol using 4-nitrobenzoylchloride. The product is then analysed by Gradient Elution High Performance Liquid Chromatography using a Polygosil Amino stationary phase with an iso-
5 hexane/ethylacetate/acetonitrile mobile phase. Detection was performed by ultra-violet absorbance. Quantification is by means of an internal normalisation technique. The results of the ethoxylate distribution and the residual free alcohol are shown in Table 1 below and are given in
10 mass percent (%m/m = %wt/wt).

Example 2

Ethoxylation of the secondary alcohol 2-undecanol

The ethoxylation of 2-undecanol was carried out using the method of Example 1 except that the reaction
15 temperature was maintained at 70°C. Measurement of the average number of moles of ethylene oxide per mole of 2-undecanol, the ethoxylate distribution and the residual free alcohol content was carried out using the same techniques as used in Example 1. The results are shown
20 in Table 1 below.

Example 3

Ethoxylation of the secondary alcohol 2-undecanol

The ethoxylation of 2-undecanol was carried out using the method of Example 1 except that the reaction
25 temperature was maintained at 130°C. Measurement of the average number of moles of ethylene oxide per mole of 2-undecanol, the ethoxylate distribution and the residual free alcohol content was carried out using the same techniques as used in Example 1. The results are shown
30 in Table 1 below.

Example 4 (Comparative)Potassium hydroxide catalysed ethoxylation of the
secondary alcohol 2-undecanol.

2-Undecanol (10.0g) and 0.2g potassium hydroxide
 5 were stirred at 130°C. Then 3 ml of toluene were added
 and removed by stripping with nitrogen (for water
 removal). To the remaining solution (9.9g), the EO was
 dosed at atmospheric pressure and stopped after the
 consumption of 16.7 g of EO. After cooling the mixture
 10 was neutralised with acetic acid. The yield of
 ethoxylated 2-undecanols was 0.083 kg EO/g KOH.

The average number of moles of EO per molecule, the
 ethoxylate distribution and the level of free alcohol
 were measured using the same methods as used in Example
 15 1. The results are shown in Table 1 below.

TABLE 1

Example No.	Ex. 1	Ex. 2	Ex. 3	Ex. 4 (comp.)
Average Ethoxylation Number (mol/mol)	5.9	6.7	6.2	6.0
Ethoxylate Distribution, $R-O-(CH_2-CH_2-O)_k-OH$:				
k=0, Residual free alcohol (%wt)	1.1	0.7	0.5	5.2
k=1 (%wt)	2.5	1.4	1.5	3.1
k=2 (%wt)	4.5	3.0	3.6	4.2
k=3 (%wt)	8.6	5.1	6.5	6.3
k=4 (%wt)	10.1	7.8	9.3	7.5
k=5 (%wt)	11.0	10.4	11.7	8.1
k=6 (%wt)	10.0	11.0	12.4	7.9
k=7 (%wt)	9.6	12.0	12.8	7.4
k=8 (%wt)	8.3	9.7	9.2	6.8
k=9 (%wt)	8.1	10.0	8.7	6.0
k=10 (%wt)	7.5	7.1	6.8	5.7
k=11 (%wt)	5.0	5.5	4.8	5.1

k=12 (%wt)	4.3	4.3	3.5	4.7
k=13 (%wt)	3.1	3.4	2.5	4.0
k=14 (%wt)	2.1	2.5	2.3	3.5
k=15 (%wt)	1.6	2.0	1.5	3.0
k=16 (%wt)	1.4	1.2	1.0	2.5
k=17 (%wt)	1.4	1.1	0.6	2.1
k=18 (%wt)	nd	1.1	0.5	1.7
k=19 (%wt)	nd	0.4	0.4	1.3
k=20 (%wt)	nd	0.3	nd	1.0
k=21 (%wt)	nd	nd	nd	0.7
k=22 (%wt)	nd	nd	nd	0.7
k=23 (%wt)	nd	nd	nd	0.7
k=24 (%wt)	nd	nd	nd	0.4
k=25 (%wt)	nd	nd	nd	0.3

nd = not determined

It can be clearly seen from Table 1 that the ethoxylated secondary alcohols prepared using a HF/boric acid catalyst have significantly reduced levels of free alcohol (k=0) and relatively narrow ethoxylate distributions (i.e. peaked distributions) compared to the ethoxylated secondary alcohol prepared using a conventional potassium hydroxide ethoxylation catalyst.

Example 5 to 7

Propylene oxide (4g) was added to an equimolar mixture of tert-butanol (0.2 mol, 14.8g), iso-propanol (12.0 g, 0.2 mol) and ethanol (0.2 mol, 9.2 g). Then 0.1 ml of trimethyl borate was added and 0.3 ml of 48% aqueous HF. The reaction started immediately. After the consumption of the propylene oxide (± 30 min) the mixture was analyzed with GLC to show a mixture comprising mono-propoxylated derivatives of tert butanol, isopropanol and ethanol.

Examples 8 to 10

Ethylene oxide was bubbled through to an equimolar mixture of tert-butanol (0.2 mol, 14.8g), iso-propanol (12.0g, 0.2 mol) and ethanol (0.2 mol, 9.2 g) containing

0.1 ml of trimethyl borate and 0.3 ml of 48% aqueous HF.
The temperature was kept below 30 °C. After $\pm$ 10 minutes
the reaction was stopped and the mixture analyzed with
GLC to show a mixture comprising mono-ethoxylated
5 derivatives of tert-butanol, isopropanol and ethanol.

C L A I M S

1. Process for preparing an alkoxyated alcohol comprising reacting a starting mono-hydroxy alcohol selected from secondary alcohols, tertiary alcohols and mixtures thereof with an alkylene oxide in the presence
5 of hydrogen fluoride and a boron-containing compound comprising at least one B-O bond.
2. Process according to Claim 1 wherein the boron-containing compound comprising at least one B-O bond is selected from boric acid, boric acid anhydrides, borate
10 esters, and mixtures thereof.
3. Process according to Claim 2 wherein the boron-containing compound comprising at least one B-O bond is selected from boric acid, boric acid anhydrides and mixtures thereof.
- 15 4. Process according to Claim 3 wherein the boron-containing compound comprising at least one B-O bond is boric acid.
5. Process according to Claim 1 or 2 wherein the boron-containing compound comprising at least one B-O bond is
20 trimethyl borate.
6. Process according to any of Claims 1 to 5 wherein the alkylene oxide is selected from ethylene oxide, propylene oxide, butylene oxide, glycidol and mixtures thereof.
- 25 7. Process according to any of Claims 1 to 6 wherein the alkylene oxide is ethylene oxide.
8. Process according to any of Claims 1 to 7 wherein the process is carried out at a temperature in the range of from 0°C to 200°C, preferably from 50°C to 130°C.

9. Process according to any of Claims 1 to 8 wherein the starting alcohol is a secondary mono-hydroxy alkanol.
10. Use of hydrogen fluoride and a boron-containing compound comprising at least one B-O bond for the
- 5 alkoxylation of a starting mono-hydroxy alcohol selected from secondary alcohols, tertiary alcohols and mixtures thereof.
11. Process for preparing an alkoxyated alcohol comprising reacting a primary mono-hydroxy alcohol with
- 10 an alkylene oxide in the presence of hydrogen fluoride and a boron-containing compound comprising at least one B-O bond, wherein is excluded a process which comprises reacting a C14/C15 alcohol with ethylene oxide in the presence of HF and trimethyl borate.
12. Process for preparing an alkoxyated alcohol comprising reacting a primary mono-hydroxy alcohol with
- 15 an alkylene oxide in the presence of hydrogen fluoride and a boron-containing compound comprising at least one B-O bond, wherein the boron-containing compound is
- 20 selected from boric acid, boric acid anhydrides, and mixtures thereof.
13. Process for preparing an alkoxyated phenol comprising reacting a starting mono-hydroxy phenol with
- 25 an alkylene oxide in the presence of hydrogen fluoride and a boron-containing compound comprising at least one B-O bond.
14. Process according to Claim 13 wherein the boron-containing compound comprising at least one B-O bond and the alkylene oxide are as defined respectively in any one
- 30 of claims 2-5 and claim 6 or 7.