PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) **International Patent Classification** 6 : **C07C 41/03, 43/11, B01J 31/26, 31/36, 31/38**	**A1**	(11) **International Publication Number:** **WO 95/11212** (43) **International Publication Date:** 27 April 1995 (27.04.95)

(21) **International Application Number:** PCT/AU94/00645

(22) **International Filing Date:** 21 October 1994 (21.10.94)

(30) **Priority Data:**

PM 1954	22 October 1993 (22.10.93)	AU
PM 1955	22 October 1993 (22.10.93)	AU

(71) **Applicant** *(for all designated States except US)*: ICI AUSTRALIA OPERATIONS PROPRIETARY LIMITED [AU/AU]; 1 Nicholson Street, Melbourne, VIC 3000 (AU).

(72) **Inventors; and**
(75) **Inventors/Applicants** *(for US only)*: DEUTSCHER, Kenneth, Reginald [AU/AU]; 25 Fraser Court, Sunbury, VIC 3249 (AU). NGIAN, Kiah, Fah [AU/AU]; 12 Kennealy Street, Surrey Hills, VIC 3127 (AU). PARR, Rodney, Walter [AU/AU]; 13 Wilma Court, Doncaster, VIC 3108 (AU). PARRIS, David [AU/AU]; F6/2 Manningham Street, Parkville, VIC 3052 (AU). TASDELEN, Esennur, Elizabeth [AU/AU]; 181 Brandon Park Drive, Mulgrave, VIC 3170 (AU).

(74) **Agent:** DAVY, John, R.; Intellectual Property Division, ICI Australia Operations Proprietary Limited, 1 Nicholson Street, P.O. Box 4311, Melbourne, VIC 3001 (AU).

(81) **Designated States:** AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ).

Published
With international search report.

(54) Title: ALKOXYLATION PROCESS

(57) Abstract

A process for the alkoxylation of organic compounds containing at least one active hydrogen which process comprises reacting said organic compound with an alkylene oxide in the presence of a catalytically effective amount of a catalyst comprising the salt of at least one element chosen from a Group Ia or Group IIa or rare earth element and an oxy-acid of at least one element chosen from a Group IVb, Group Vb or Group VIb element or mixtures thereof wherein said catalyst is supported on an inert or active support and/or comprises hydrophobic groups. An alkoxylation catalyst comprising the salt of at least one element chosen from a Group Ia or Group IIa or rare earth element and an oxy-acid of at least one element chosen from a Group IVb, Group Vb or Group VIb element or mixtures thereof wherein said catalyst comprises hydrophobic groups and is supported on an inert or active support.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria
AU	Australia
BB	Barbados
BE	Belgium
BF	Burkina Faso
BG	Bulgaria
BJ	Benin
BR	Brazil
BY	Belarus
CA	Canada
CF	Central African Republic
CG	Congo
CH	Switzerland
CI	Côte d'Ivoire
CM	Cameroon
CN	China
CS	Czechoslovakia
CZ	Czech Republic
DE	Germany
DK	Denmark
ES	Spain
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
GE	Georgia
GN	Guinea
GR	Greece
HU	Hungary
IE	Ireland
IT	Italy
JP	Japan
KE	Kenya
KG	Kyrgystan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
KZ	Kazakhstan
LI	Liechtenstein
LK	Sri Lanka
LU	Luxembourg
LV	Latvia
MC	Monaco
MD	Republic of Moldova
MG	Madagascar
ML	Mali
MN	Mongolia
MR	Mauritania
MW	Malawi
NE	Niger
NL	Netherlands
NO	Norway
NZ	New Zealand
PL	Poland
PT	Portugal
RO	Romania
RU	Russian Federation
SD	Sudan
SE	Sweden
SI	Slovenia
SK	Slovakia
SN	Senegal
TD	Chad
TG	Togo
TJ	Tajikistan
TT	Trinidad and Tobago
UA	Ukraine
US	United States of America
UZ	Uzbekistan
VN	Viet Nam

ALKOXYLATION PROCESS

The present invention relates to the preparation of alkoxylation products by the catalysed condensation reaction of epoxides (alkylene oxides) and organic compounds having at least one active hydrogen.

A wide variety of alkoxylation products prepared by the condensation reaction of alkylene oxides with organic compounds having at least one active hydrogen are of industrial significance. The products of condensation of an alkylene oxide, and particularly ethylene oxide or propylene oxide or mixtures thereof, and an alcohol or a phenol are well known surface active agents. Other condensation products find application as solvents, and functional fluids. Such alkoxylation products are conventionally prepared by the reaction of at least one active hydrogen compound with an alkylene oxide (epoxide) in the presence of an alkaline or acidic catalyst. The average oxyalkylene chain length of such alkoxylation products depends on the mole ratio of epoxide to active hydrogen containing organic compound used and the reaction results in a mixture of different compounds having a range of oxyalkylene chain lengths and hence molecular weights.

It has long been recognised as desirable to control the molecular weight distribution of alkoxylates in order to be able to take best advantage of the properties of alkoxylates with specific alkylene oxide chain lengths. Acidic catalysts are known to tend to give narrower molecular weight distributions than alkaline catalysts but also promote side reactions which lead to the formation of undesired by-products. The commonly used alkaline catalysts are known to give broad molecular weight distribution but few by-products and are generally the alkoxylation catalysts used in industry today. Such catalysts include the alkali metal hydroxides and alkoxides and in particular sodium and potassium hydroxide.

In recent years much attention has been focused on developing catalysts which are as efficient as the alkali metal hydroxides but give products with narrow molecular weight distribution. United States Patent No. 4453023 describes a process which employs a catalyst comprising a barium compound and a promoter selected from various oxides and acids of phosphorus, carbon dioxide and oxalic acid. International patent application publication number WO85/00365 describes use of an alkoxylation catalyst comprising the reaction product of calcium oxide or calcium hydroxide and an inorganic oxy-acid derivative with an organic compound. European patent publication numbers 361616 to 361620 describe alkoxylation catalysts prepared by reacting various Group IIA, IIIB and other metal sources with an organic activator to give a composition which is further reacted with a di or poly-valent metal or metal containing compound such as divalent or polyvalent oxy-acid salts. European patent publication number 361621 describes the use of calcium sulphate as an alkoxylation catalyst. European patent publication number 398450 describes the use of barium phosphate as an alkoxylation catalyst.

In International Patent Application No PCT/AU 93/00174 we teach that salts of the Group Ia, IIa and the rare earth elements with the oxy-acids of the Group IVb, Vb and VIb elements may be used as catalysts in alkoxylation reactions and that these catalysts give the desired features of a narrow distribution of alkoxylation species and efficient reaction rates. Such catalysts have been found to be very effective in the preparation of both lower and higher alkoxylates with narrow molecular weight distributions. Moreover, when such catalysts are in the form of finely divided solids they may be recovered by a suitable means and recycled.

We have now found that the catalyst used in the process taught in PCT/AU 93/00174 may be used in a manner which facilitates their recovery and recycling while maintaining their activity and narrow product molecular weight distribution by supporting them on inert or active support material in the presence of alkoxylation reactants and products.

Furthermore, we have now found that the rate of reaction in the process taught in PCT/AU 93/00174 may be increased, without loss of narrow product molecular weight distribution, by the use of catalysts which have been modified by introduction of hydrophobic groups.

Accordingly, the invention provides a process for the alkoxylation of organic compounds containing at least one active hydrogen which process comprises reacting said organic compound with an alkylene oxide in the presence of a catalytically effective amount of a catalyst comprising the salt of at least one element chosen from a Group Ia or Group IIa or rare earth element and an oxy-acid of at least one element chosen from a Group IVb, Group Vb or Group VIb element or mixtures thereof wherein said catalyst is supported on an inert or active support and/or comprises hydrophobic groups.

The invention further provides an alkoxylation catalyst comprising the salt of at least one element chosen from a Group Ia or Group IIa or rare earth element and an oxy-acid of at least one element chosen from a Group IVb, Group Vb or Group VIb element or mixtures thereof wherein said catalyst comprises hydrophobic groups and is optionally supported on an inert or active support.

As used herein the term "rare earth element" includes scandium, yttrium, lanthanum and elements of atomic numbers 58 through to 71 (the lanthanides).

The term "inert support" is used to mean a solid support material which is essentially inert in the presence of alkoxylation reactants and products. Inert support materials may be chosen from the wide range of catalyst supports known in the art for the support of catalysts provided the support material is essentially inert in the presence of alkoxylation reactants and products. The catalyst may be on the external surface of the support or, in the case of a porous support, incorporated into the support on the internal surfaces of the pores. Alternatively the catalyst may be incorporated into the matrix of a porous support material.

Suitable inert support materials may be chosen from the wide range of inorganic material known in the art for the support of catalysts provided the support material is essentially inert in the presence of alkoxylation reactants and products. Suitable supports may be chosen from inorganic material such as, for example, porous and non-porous alumina, silica, silica-alumina, titania, zirconia, magnesia, diatomaceous earth and similar materials, inert salts of Group IIa and rare earth elements, and mixtures thereof. Other suitable supports include polymeric organic materials such as, for example, polystyrene, polyethylene, polypropylene, polyimide and grafted derivatives thereof.

Support materials can also be chosen from materials that are active in the presence of alkoxylation reactants and products, "active supports", provided that their activity does not contribute to the formation of undesirable products or by-products. However, these active supports are not primarily chosen for their efficacy as alkoxylation catalysts but they are primarily chosen on their merits as supports. Examples of such supports might include weakly acidic or basic, simple or mixed oxides or hydroxides such as magnesium oxide, active (gamma) alumina or silica-alumina, or materials known to be active in the alkoxylation reaction used in their active or partially or fully deactivated form. Preferably these supports are chosen from oxides, hydroxides or salts of Group Ia, IIa, IVB, VB or VIB, rare earth elements or mixtures thereof. Most preferably they are chosen from the oxides, hydroxides and salts of Group IVB or mixtures thereof and their mixtures with the elements of Group IIIB, including self supported catalyst.

The catalyst may be on the external surface of the active support or, in the case of a porous support, incorporated into the support on the internal surfaces of the pores. Alternatively the catalyst may be incorporated into the matrix of a porous support material.

The term "hydrophobic groups" is used herein to mean an organic radical containing a C_2 to C_{30} saturated or unsaturated, branched or unbranched, substituted or unsubstituted hydrocarbon chain. Examples of such organic radicals are those which may be derived from the so-called fatty acids, fatty alcohols, fatty amines, fatty amides and their synthetic analogues and homologues, and polymers comprising carboxylic acid, alcohol, amine or amide groups, alkylphenols and the thio analogues of such compounds and/or polymers.

Hydrophobic groups may be incorporated in the catalysts of the present invention by treatment of a preprepared catalyst comprising the salt of at least one element chosen from a Group Ia or Group IIa or rare earth element and an oxy-acid of at least one element chosen from a Group IVb, Group Vb or Group VIb element or mixtures thereof with a precursor of an organic radical comprising an hydrophobic group. Alternatively, hydrophobic groups may be incorporated in the catalysts of the present invention by preparation of the catalyst of the present invention in the presence of a precursor of an organic radical comprising an hydrophobic group.

Examples of precursors of organic radicals comprising an acyl group include the C_2 to C_{30} carboxylic acids such as acetic acid, propionic acid, butyric acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, dodecanoic acid, tridecanoic acid, tetradecanoic acid, pentadecanoic acid, hexadecanoic acid, heptadecanoic acid, octadecenoic acid, nonadecanoic acid, eicosanoic acid, docosanoic acid, cis-9-octadecenoic, tetracosanoic acid, 2-hexadecanoic acid, cis-9-octadecenoic acid, trans-9-octadecenoic acid, trans-9-

octadecenoic acid, 9,12-octadecadianoic acid, 9,12,15-octadecatrienoic acid and 12-hydroxyoctadecanoic acid, salts thereof including, for example, their alkali metal and alkaline earth metal salts, their acid halide derivates and their acid amide derivatives and mixtures thereof. Further examples of precursors of organic radicals include polymers functionalised with, for example acyl, hydroxy or amine groups and derivatives thereof such as, for example, the "HYPERMER" range of dispersants ("HYPERMER" is a Trade Mark of Imperial Chemical Industries PLC).

Examples of precursors of organic radicals comprising an alkoxy group include the C_2 to C_{30} alcohols such as ethanol, propanol, butanol, pentanol, hexanol, heptanol, octanol, nonanol, decanol, undecanol, dodecanol, tridecanol, tetradecanol, pentadecanol, hexadecanol, heptadecanol, octadecanol, nonadecanol, 2-hexadecanol, eicosanol, docosanol, tetracosanol, 2-hexadecanol, cis-9-octadecenol, trans-9-octadecenol, 9,12-octadecadienol, 9,12,15-octadecatrienol, 12-hydroxyoctadecanol, mixtures thereof and the alkali metal salts thereof.

Examples of precursors of organic radicals comprising an amine group include the C_2 to C_{30} alkylamines such as propylamine, butylamine, pentylamine, hexylamine, heptylamine, octylamine, nonylamine, decylamine, undecylamine, dodecylamine, tridecylamine, tetradecylamine, pentadecylamine, hexadecylamine, heptadecylamine, octadecylamine and mixtures thereof.

Examples of precursors of organic radicals comprising a phenoxy group include phenol, C_2 to C_{30} alkylphenols, their alkali metal salts and mixtures thereof.

Preferably the catalyst component of the supported and/or hydrophobic catalysts used in the invention and in the process of the invention are selected from compounds of the general formula I:

$$M_m(XO_n) \qquad \text{I}$$

wherein:

M is selected from the group consisting of Li, Na, K, Mg, Ca, Sr, Ba, Sc, Y, La, Ce and Nd and mixtures thereof;
X is selected from the group consisting of Ti, Zr, Hf, Nb, Mo, W and mixtures thereof;
m and n are selected to satisfy valency requirements, n being typically 2.0 to 6.0 and m being typically 0.2 to 2.0.

Preferred values for M include K, Ca, Sr, Ba, La, Y and Nd and mixtures thereof.

Preferred values for X include Ti, Zr, Hf, Mo, Nb and mixtures thereof.

Preferred compounds of formula I which may be used as the catalyst component of the catalysts used in the process of the present invention include barium titanate, barium zirconate, strontium titanate, strontium zirconate, barium strontium titanate, lanthanum titanate, potassium lanthanum titanate, yttrium titanate, lanthanum zirconate, lanthanum hafnate, barium strontium titanate zirconate, barium niobate, lanthanum molybdate, neodymium titanate and calcium titanate.

More preferred compounds of formula I which may be used as the catalyst component of the catalysts used in the process of the present invention include lanthanum titanate, barium titanate, barium strontium titanate, yttrium titanate, lanthanum zirconate, barium zirconate, lanthanum hafnate, barium strontium titanate zirconate and neodymium titanate.

The supported catalyst used in the process of the present invention may be prepared by any suitable technique known in the art for the preparation of supported catalysts. Such techniques include: preparation of the catalyst in the presence of the support with incorporation of the catalyst product onto the support or, in the case of a porous support, into the pores of the support material; deposition of the catalyst onto the surface of the support, or in the case of a porous support, into the pores of the support material; impregnation of a porous support; coprecipitation of support and catalyst; comulling of support and catalyst; spray-drying; pelletisation or any combination of such conventional art techniques.

The preparation of the supported catalyst can be carried out in one or more steps. It may be preferred to incorporate only one of the catalyst components in a particular step. It may also be preferred to add a catalyst component in portions over several discreet steps and under differing conditions.

Control over granule size distribution of self supported catalysts is desirable for making industrially useful, that is, suitable for use in particular plants, catalysts. This control can be exercised by employing the techniques well known to those skilled in the art of sol-gel manufacture of mixed metal oxides such as those described in Hubert-Pfalzgraf, LG, *New Journal of Chemistry*, 1987, 11, p663 or Livage, J, and Sanchez, C, *Journal of Non-Crystalline Solids*, 1992, 145, p11 or Livage, J, Sanchez, C, and Toledano, P, *Mat. Res. Soc. Symp. Proc.*, 1992, 272, p3.

The catalyst component of the supported and/or hydrophobic catalyst of the present invention may comprise from about 0.5 to 100% by weight of the total supported catalyst. Preferably the catalyst component comprises from 10 to 60% of the total supported catalyst.

The process of the present invention may be applied to alkoxylation using a range of alkylene oxides. Examples of alkylene oxides include ethylene oxide, propylene oxide, the butylene oxides, glycidol, epichlorohydrin, cyclohexene oxide, cyclopentene oxide and styrene oxide. The process of the invention is particularly useful in ethoxylation reactions using ethylene oxide and propoxylation reactions using propylene oxide and alkoxylation using mixed ethylene and propylene oxides.

The process of the present invention may be used in the alkoxylation of a wide range of organic compounds containing reactive hydrogen. Examples of such compounds include alcohols, thiols, phenols, thiophenols, carboxylic acids, amides and amines. Examples of alcohols which may be alkoxylated using the process of the present invention include primary and secondary C_1-C_{30} straight and branch chain alcohols, cycloaliphatic alcohols, glycols, polyethylene glycols, polypropylene glycols, and polyhydric alcohols such as pentaerythritol and glycerol.

Alcohols and phenols, including alkyl substituted phenols, are preferred organic compounds containing reactive hydrogen which may be alkoxylated using the process of the present invention. Preferred alcohols include C_1-C_{30} alcohols with C_6-C_{20} alcohols amongst those most preferred. Preferred phenols include phenol and C_1-C_{20} alkyl substituted phenols such as, for example, 4-nonylphenol and 4-decylphenol.

The amount of catalyst used in the process of the present invention depends to a large extent on the nature of the catalyst used and the organic compound containing reactive hydrogen and the alkylene oxide which are being reacted. Hence the amount of hydrophobic and/or supported catalyst used is that amount which is catalytically effective in carrying out the alkoxylation reaction at the rate and with the selectivity desired. Typically the catalyst level may vary in the range of from 0.1 ppm to 25 percent by weight based on the weight of the organic compound containing reactive hydrogen. Preferably the catalyst is in the range of from 0.5 to 20% by weight of the organic compound containing reactive hydrogen.

In a preferred embodiment the process of the current invention for alkoxylation of organic compounds comprises the steps of;

adding a hydrophobic and/or supported catalyst to the organic compound containing at least one active hydrogen;

heating the reactor containing said organic compound;

supplying alkylene oxide to said organic compound and hydrophobic catalyst at a process temperature of between 50 and 250°C and at a process pressure above atmospheric pressure; and isolating the alkoxylation products.

The process of the present invention may be carried out using batch or continuous processing techniques. Batch processing may be carried out in a stirrer equipped reactor using conventional techniques for catalyst contacting and separation. Continuous processing may be carried out using any of the known techniques for contacting fluid reactants with solid catalysts, such as, for example, a fixed catalyst bed or a fluid catalyst bed.

One of the advantages of the supported catalyst and the supported hydrophobic catalysts used in the process of the present invention over prior art unsupported catalysts is the ease with which they may be removed from the reaction mixture during isolation of the reaction products and the ease with which they can be incorporated into a continuous processing facility. The ease of removal from the reaction mixture of the supported catalysts used in the process of the present invention greatly facilitates product isolation and catalyst recycling in batch processing operations.

A particular advantage of the supported catalysts and supported hydrophobised catalysts of the current invention are their recyclability. Many of the catalysts may be recycled at least ten times without significant loss of selectivity or activity.

The temperature which the process of the present invention is carried out will depend upon a number a factors including the heating and cooling facilities available in the reaction vessel and the pressure at which the reaction vessel may be operated. However, in general, a temperature in the range of from 50 to 250°C is satisfactory and a temperature in the range of from 80 to 200°C may be preferred.

The pressure at which the process of the present invention is carried out will depend to a large extent on the alkylene oxide used and the temperature at which the reaction is carried out. However, preferably the process of the present invention is carried out at a pressure above atmospheric pressure. In practice a reaction pressure of between 300 kPa and 700 kPa with an alkylene oxide partial pressure of between 100 and 500 kPa has been found to be suitable.

The reaction time required for the process of the present invention is dependent upon the nature of the reactive hydrogen compound and the nature of the alkylene oxide used, the reaction temperature and pressure and the catalyst and quantity of the catalyst used. In practice, reaction times may vary from 15 minutes to approximately 20 hours.

Surprisingly, it has been found that certain hydrophobic catalysts used in the process of the present invention, including hydrophobic lanthanum titanate, provide a reaction rate faster than that obtained using lanthanum titanate and produce products having a molecular weight distribution comparable with the narrow range obtained using lanthanum titanate. Surprisingly, it has been found that certain hydrophobic catalysts used in the process of the present invention, including hydrophobic lanthanum titanate, provide a reaction rate comparable to that obtained with potassium hydroxide as well as producing narrow molecular weight distribution products.

Surprisingly, it has also been found that certain supported catalysts used in the process of the present invention provide a reaction rate comparable to that obtained with potassium hydroxide and produce products having a molecular weight distribution comparable with the narrow range obtained using a catalyst in the absence of a support.

The supported and/or hydrophobic catalysts used in the present invention are in the form of solids. Therefore, in batch processing, after the reaction has been completed and the product cooled, the supported catalyst may be recovered from the final product by any means suitable for the removal of solids from a reaction mixture. For example, depending on the particle size of the solid and the viscosity of the product, the catalyst may be removed by filtration, centrifugation, extraction or suitable like means.

A supported hydrophobic catalyst for use in the process of the present invention may be prepared by any suitable technique known in the art for the preparation of supported catalysts. Such techniques include: preparation of the catalyst in the presence of the support with incorporation of the catalyst product onto the support or in the case of a porous support, into the pores of the support material; deposition of the catalyst onto the surface of the support, or in the case of a porous support, into the pores of the support material; impregnation of a porous support; coprecipitation of support and catalyst; comulling of support and catalyst; spray-drying; pelletisation or any combination of such conventional art techniques. As hereinbefore noted, hydrophobic groups may be incorporated in the catalyst of the present invention by reaction of a preprepared catalyst, and hence a preprepared supported catalyst, with a precursor of an organic radical containing an hydrophobic group or by preparing the catalyst, and hence the supported catalyst, in the presence of a precursor of an organic radical containing an hydrophobic group.

It should be noted, that although not essential for the process of the present invention, the supported catalyst used for the process of the present invention may also contain other components including impurities resulting from the preparation of the catalyst and introduced components which may be added to promote or modify catalyst activity and/or selectivity. For example, the supported catalyst used in the process of the present invention may be treated with a reagent to introduce hydrophobic sites on the supported catalyst and make it more compatible with a hydrophobic organic compound reactant containing at lest one active hydrogen. Introduction of hydrophobic sites may be achieved by treating the supported catalyst with a reagent which incorporates hydrophobic groups such as hydrocarbon chains onto the supported catalyst. Suitable reagents may be chosen from those which will incorporate fatty alcohol, fatty acid, fatty amine, fatty amide and the like radicals onto the supported catalyst to make it hydrophobic in character.

Surprisingly, the process of the present invention provides molecular weight distributions for both lower and higher alkoxylates that are narrower than those which would be expected from alkoxylation reactions using conventional alkali metal hydroxide catalysts.

The invention is now illustrated by, but not limited to, the following Examples.

Example 1

Lanthanum titanate catalyst supported on diatomaceous earth was prepared by the following procedure.

A suspension of CELITE (17.4 grams, CELITE is the trademark of the Manville Corporation) in lanthanum nitrate solution (25.2 grams of $La(NO_3)_35H_2O$, 0.0600 moles of La, in 1000 ml of deionised water) was vigorously stirred to allow the solution to penetrate the CELITE and heated to 50°C. Ammonia solution (100 ml, 28% w/w) was added to the mixture over 15 minutes, followed by the addition of a solution of titanium alkoxide (26.7 grams of $Ti(OR)_4$ where R = ^{i}Pr (80%), R = ^{n}Bu (20%), 0.0915 moles of Ti) in isopropanol (300 ml) over 135 minutes at 50°C, whilst maintaining vigorous stirring.

The reaction mixture was then heated at 50°C for an additional hour, cooled and the white solid was isolated by filtration and washed with deionised water. The solid was then dried at 400°C for 16 hours to afford 34.1 grams of white powder.

An alkoxylation process in accordance with the invention was conducted by the following procedure. The alkylene oxide reactant for this process embodiment consisted of ethylene oxide. The active hydrogen containing reactant consisted of NACOL-10-99 alcohol (NACOL is a registered trademark of Condea Chemie) characterised as a primary, linear alkanol having ten carbon atoms (>99%) or PICOL-1095 alcohol (PICOL is a registered trademark of Pilipinas KAO) characterised as a primary, linear alkanol having ten carbon atoms (>95%).

Initially, 14.3 grams of the diatomaceous earth supported lanthanum titanate, prepared as described above and containing 7.15 grams of lanthanum titanate, was added to 249 grams of NACOL-10-99 alcohol, and the mixture was transferred to a two litre autoclave reactor maintained under nitrogen atmosphere. The autoclave and its contents were then heated at 100-110°C under vacuum with nitrogen sparging for 80 minutes to drive off any water. The mixture was then heated to 150°C and the autoclave pressurised to 40 kPa with nitrogen. Ethylene oxide was then introduced into the reactor to a total pressure of 400 kPa. Alkoxylation (ethoxylation) commenced immediately. Additional ethylene oxide was supplied on demand to maintain a pressure of 400 kPa and temperature maintained between 150 to 160°C.

A total of 210 grams of ethylene oxide was taken up over a period of 85 minutes. The reactor was maintained at temperature for an additional 30 minutes to consume unreacted ethylene oxide.

The product was analysed by GLC techniques and found to have an average adduct number of 3.1. The ethylene oxide adduct distribution of the product is presented in Figure 1.

Further ethoxylation of this product (323 grams) was carried out following the above general procedure. A total of 245 grams of ethylene oxide was taken up over a period of 85 minutes. The reactor was maintained at temperature for an additional one hour to consume unreacted ethylene oxide. The product was analysed by GLC techniques to have an average adduct number of 7.6. The ethylene oxide adduct distribution of the product is presented in Figure 2.

Comparative Example 1a

Unsupported lanthanum titanate was prepared following the procedure of Example 1, however, without the addition of diatomaceous earth.

An alkoxylation process was carried out under the same general procedures of Example 1 except for the use of unsupported lanthanum titanate as alkoxylation catalyst. A total of 249 grams of NACOL-10-99 alcohol and 7.10 grams of the unsupported lanthanum titanate were used. At a reaction temperature of 150-160°C, a total of 210 grams of ethylene oxide was added over a period of 95 minutes. The product was analysed by GLC techniques and found to have an average adduct number of 3.0. The ethylene oxide adduct distribution of the product has been compared with that from Example 1 in Figure 3. This comparison illustrates that a narrow product molecular weight distribution and activity has been maintained on supporting lanthanum titanate on diatomaceous earth.

Comparative Example 1b

An alkoxylation process was carried out under the same general procedures of Example 1 except for the use of diatomaceous earth as alkoxylation catalyst. A total of 249 grams of NACOL-10-99 alcohol and 7.15 grams of CELITE were used. At a reaction temperature of 150-160°C, less than 40 grams of ethylene oxide was taken up over a period of 4 hours. This comparative example illustrates that the diatomaceous earth used to support lanthanum titanate in Example 1 is "inert" under alkoxylation conditions.

Example 2

Lanthanum titanate catalyst supported on hydrous titania was prepared by the following procedure.

A solution of lanthanum nitrate (5.4 grams of $La(NO_3)_3 .6H_2O$, 0.0125 moles of La) and titanium alkoxide (9.90 grams of $Ti(OR)_4$ where R = ^{i}Pr (80%), R = ^{n}Bu (20%), 0.0340 moles of Ti) in isopropanol (17.8 grams) was added to the hydrous titania (5.40 grams). This mixture was tumbled to allow the solution to penetrate the hydrous titania particles and partially dried in air at 95-100°C. The semi-dry solid was then exposed to ammonia vapour for 16 hours, resuspended in water (100 ml) and filtered. The white solid was washed with water (300 ml) and isopropanol (100 ml). The wet catalyst was dehydrated in the presence of PICOL-1095 alcohol at 100-110°C under vacuum prior to carrying out the alkoxylation reaction.

An alkoxylation process in accordance with the invention was conducted under the same general procedures described for Example 1, using as alkoxylation catalyst the hydrous titania supported lanthanum titanate prepared as described above. A total of 200 grams of PICOL-1095 alcohol and 12.8 grams of the "wet" hydrous titania supported lanthanum titanate (51% w/w total solids containing 47% w/w lanthanum titanate) were used. At a reaction temperature of 155-165°C, a total of 170 grams of ethylene oxide was added over a period of 43 minutes. The product was analysed by GLC techniques and found to have an average adduct number of 3.1. The ethylene oxide adduct distribution of the product is presented in Figure 4.

Further ethoxylation of this product (141 grams) was carried out following the above general procedure. A total of 105 grams of ethylene oxide was taken up over a period of 60 minutes. The product was analysed by GLC techniques and found to have an average adduct number of 6.9. The ethylene oxide adduct distribution of the product is present in Figure 5.

Comparative Example 2a

An alkoxylation process in accordance with the invention was conducted under the same general procedures described for Example 1 except hydrous titania was used as alkoxylation catalyst. A total of 201 grams of PICOL-1095 alcohol and 3.45 grams of hydrous titania were used. At a reaction temperature of 155-165°C, a total of 170 grams of ethylene oxide was added over a period of 390 minutes. The product was analysed by GLC techniques and found to have an average adduct number of 2.1. This comparative example illustrates that the hydrous titania used to support lanthanum titanate in Example 2 has low activity under typical alkoxylation conditions.

Example 3

Lanthanum titanate catalyst supported on hydrous zirconia was prepared by the following procedure.

A solution of lanthanum nitrate (8.5 grams of $La(NO_3)_3.6H_2O$, 0.0197 moles of La) and titanium alkoxide (15.5 grams of $Ti(OR)_4$ where R = ^{i}Pr(80%), R = ^{n}Bu(20%), 0.0532 moles of Ti) in ethanol (60 ml) was added to the hydrous zirconia (8.90 grams). This mixture was stirred to allow the solution to penetrate the hydrous zirconia particles and partially dried in air at 95-100°C. The semi-dry solid was then exposed to ammonia vapour for 16 hours, resuspended in water (200 ml) and filtered. The white solid was washed with water (500 ml) and then isopropanol (100 ml). The wet catalyst was dehydrated in the presence of PICOL-1095 alcohol at 100-110°C under vacuum prior to carrying out the alkoxylation reaction.

An alkoxylation process in accordance with the invention was conducted under the same general procedures described for Example 1, using as alkoxylation catalyst the hydrous zirconia supported lanthanum titanate prepared as described above. A total of 254 grams of PICOL-1095 alcohol and 26.7 grams of the "wet" hydrous zirconia supported lanthanum titanate (43% w/w total solids containing 46% w/w lanthanum titanate) were used. At a reaction temperature of 155-165°C, a total of 210 grams of ethylene oxide was added over a period of 42 minutes. The product was analysed by GLC techniques and found to have an average adduct number of 3.0. The ethylene oxide adduct distribution of the product is presented in Figure 6.

Example 4

Self supported lanthanum titanate was prepared by the following pelletisation procedure.

Stage 1

Lanthanum nitrate (21.7 grams of $La(NO_3)_3 .6H_2O$, 0.0501 moles of La) was dissolved in deionised water (300 ml) and the pH of the solution adjusted to 2.9 with nitric acid. A solution of titanium alkoxide (39.5 grams of $Ti(OR)_4$ where R = ${}^iPr$ (80%), R = ${}^nBu$ (20%), 0.135 moles of Ti) in isopropanol (70 grams) was added over 15 minutes to the stirred lanthanum nitrate solution, allowing the temperature to rise to 55°C. A solution of triethanolamine (20.9 grams; 0.139 moles) in water (21 ml) was then added to the mixture and stirring maintained for 15 minutes at 55-65°C. This was followed by the addition of ammonia solution (40 ml, 28% w/w) over 10 minutes. The mixture was stirred for a further 20 minutes at 55°C, cooled overnight and then centrifuged. The white precipitate was resuspended in methanol (500 ml) and recentrifuged. This procedure was repeated with isopropanol (300 ml). The white solid was dried initially in a vacuum oven at 50°C for 10 minutes then in a furnace at 200°C for 3 hours.

Stage 2

Using a die presser, a sample of the lanthanum titanate isolated from Stage 1 was pressed to 2 tonne/mm^2 at ambient temperature for 5 minutes, then heat pressed to 2 tonne/mm^2 at 120°C for 15 minutes.

An alkoxylation process in accordance with the invention was conducted under the same general procedures described for Example 1, using as alkoxylation catalyst the pelletised lanthanum titanate prepared as described above. A total of 150 grams of PICOL-1095 alcohol and 2.00 grams of the pelletised lanthanum titanate were used. At a reaction temperature of 155-165°C, a total of 125 grams of ethylene oxide was added over a period of 96 minutes. The product was analysed by GLC techniques and found to have an average adduct number of 3.0. The ethylene oxide adduct distribution of the product is presented in Figure 7.

In a further example, a sample of the lanthanum titanate isolated from Stage 1 was heat pressed to 1 tonne/mm^2 at 120°C for 15 minutes. An alkoxylation process in accordance with the invention was conducted under the same general procedures described for Example 1, using as alkoxylation catalyst this sample of pelletised lanthanum titanate. A total of 151 grams of PICOL-1095 alcohol and 2.00 grams of the pelletised lanthanum titanate were used. At a reaction temperature of 155-165°C, a total of 125 grams of ethylene oxide was added over a period of 112 minutes. The product was analysed by GLC techniques and found to have an average adduct number of 2.9. The ethylene oxide adduct distribution of the product is presented in Figure 8.

Example 5

Self supported barium titanate was prepared by the following pelletisation procedure.

A solution of tetrabutyltitanate (30.6 grams, 0.0899 moles of Ti) in isopropanol (150 ml) was added dropwise over 45 minutes to a well stirred solution of barium hydroxide (31.5 grams of $Ba(OH)_2.8H_2O$, 0.100 moles of Ba) in deionised water (100 ml) at 50-60°C. The resulting mixture was heated at 50-60°C for an additional 20 minutes, the white precipitate allowed to settle and the supernatant liquid decanted. The precipitate was washed with deionised water several times and dried at 400°C for 3 hours.

Using a die presser, a sample of this dried barium titanate was pressed to 5 tonne/mm^2 at ambient temperature for 15 minutes. The pelletised barium titanate was further dried at 400°C for 4 hours.

An alkoxylation process in accordance with the invention was conducted under the same general procedures described for Example 1, using as alkoxylation catalyst the pelletised barium titanate prepared as described above. A total of 198 grams of NACOL-10-99 alcohol and 4.40 grams of the pelletised barium titanate were used. At a reaction temperature of 155-160°C, a total of 165 grams of ethylene oxide was added over a period of 14.6 hours. The product was analysed by GLC techniques and found to have an average adduct number of 3.0. The ethylene oxide adduct distribution of the product is presented in Figure 9.

Example 6

Hydrophobic lanthanum titanate was prepared by the following procedure. Ammonia solution (100 ml, 28% w/w) was added to a vigorously stirred solution of lanthanum nitrate (25.2 grams of $La(NO_3)_3.5H_2O$, 0.0600 moles of La) in deionised water (1000 ml) at 47-58°C, over 15 minutes. A solution of titanium alkoxide (46.1 grams of $Ti(OR)_4$ where R = ^{i}Pr (80%), R = ^{n}Bu (20%), 0.158 moles of Ti) in isopropanol (530 ml) was then added over 2 hours to the resulting mixture at 58°C, whilst maintaining vigorous stirring.

The reaction mixture was then heated at 58°C for an additional 2 hours, cooled and the precipitate isolated by filtration and washed with deionised water. The solid was then dried at 200°C for 17 hours to afford 24.4 grams of a white powder.

The preparation of lanthanum titanate as described above was repeated, except the catalyst drying temperature was varied.

Alkoxylation processes were carried out under the same procedures and conditions of Example 1 using these catalysts dried at different temperatures.

Table:
Example 6 - Alkoxylation Time vs Lanthanum Titanate Drying Temperature.

Drying Temperature (°C)	110	160	200	250	350
Alkoxylation Time (min/mol EO)	10	10	12	17	18

Hydrophobic groups contained in the catalyst are believed to be progressively displaced at drying temperatures of 200°C and above, resulting in a decrease in catalytic activity (Reference: Yoldas, BE, *Journal of Materials Science,* 1986, 21, p1087).

Example 7

The lanthanum titanate prepared as described in Example 6 (dried at 200°C) was further hydrophobised by the following procedure. A slurry of a sample of the lanthanum titanate (7.13 grams) in isopropanol (200 ml) was added to a stirred solution of n-decanoic acid (13.0 grams, 0.0755 moles) in isopropanol (150 ml) which had been treated with ammonia solution (5 ml, 28% w/w), under an atmosphere of nitrogen. The mixture was then heated at 70°C for 3 hours, cooled and the solid was isolated by filtration and washed with isopropanol (100 ml). The catalyst obtained was used directly in the alkoxylation process. Any residual isopropanol was removed during the dehydration step of the alkoxylation process.

An alkoxylation process in accordance with the invention was conducted under the same general procedures described in Example 1, using as alkoxylation the hydrophobised lanthanum titanate. A total of 250 grams of NACOL-10-99 alcohol (250 grams) and 7.59 grams of the hydrophobic lanthanum titanate were used. At a reaction temperature of 150-160°C, a total of 550 grams of ethylene oxide was taken up over a period of 59 minutes. The product was analysed by gas chromatography and found to have an average adduct number of 7.7. The ethylene oxide adduct distribution of the product is presented in Figure 10.

Comparative Example 7a

An alkoxylation process was carried out under the same procedures and conditions of Example 7 except for the use of the lanthanum titanate catalyst isolated from Example 6 and dried at 200°C. This example is provided to illustrate the distinction between the invention and "untreated" lanthanum titanate with respect to catalytic activity.

A total of 250 grams of NACOL-10-99 alcohol and 7.17 grams of lanthanum titanate were used. At a reaction temperature of 160°C, a total of 550 grams of ethylene oxide was taken up over 89 minutes. The product was analysed by GLC techniques and found to have an average adduct number of 7.4. The ethylene oxide adduct distribution of the product is presented in Figure 12. A comparison of catalytic activity of the hydrophobised and "untreated" lanthanum titanate catalysts is presented in Figure 11.

Comparative Example 7b

Lanthanum titanate was prepared using titanyl sulfate in place of the titanium alkoxide. This comparative example illustrates that incorporation of hydrophobic groups in the catalyst by the use of a hydrophobic titanium alkoxide precursor increases the rate of alkoxylation reaction.

Titanyl sulfate (36.9 grams of $TiOSO_4xH_2O$ containing 0.158 moles of Ti) was dissolved in deionised water (400 ml) by stirring the mixture over 2 hours.

Ammonia solution (100 ml, 28% w/w) was added to a vigorously stirred solution of lanthanum nitrate (25.2 grams of $La(NO_3)_3.5H_2O$, 0.0600 moles of La) in deionised water (1000 ml) at 58-60°C over 15 minutes. The titanyl sulfate solution was then added over 2 hours to the resulting mixture at 60°C, whilst maintaining vigorous stirring. The reaction mixture was then heated at 60°C for an additional 2 hours, cooled and the precipitate isolated by filtration. The precipitate was resuspended in ammonium carbonate solution, refiltered and exhaustively washed with water, followed by isopropanol. The solid was then dried at 160°C for 17 hours to afford 24.9 grams of a white powder.

An alkoxylation process in accordance with the invention was conducted under the same general procedures described for Example 1, using as alkoxylation catalyst the lanthanum titanate prepared as described above. A total of 250 grams of NACOL-10-99 alcohol and 7.13 grams of lanthanum titanate were used. At a reaction temperature of 160°C, a total of 210 grams of ethylene oxide was taken up over a period of 84 minutes, corresponding to an alkoxylation rate of 28 min/mol EO. This is in comparison to a rate of 10 min/mol EO obtained with the catalyst prepared from titanium alkoxide, as illustrated in Example 6. The product was analysed by GLC techniques and found to have an average adduct number of 2.8. The ethylene oxide adduct distribution of the product is presented in Figure 13.

Example 8

Another example of a hydrophobic lanthanum titanate catalyst was prepared by the following procedure.

Titanium alkoxide (316 grams of $Ti(OR)_4$ where R = ^{i}Pr (80%), R= ^{n}Bu (20%), 1.08 moles of Ti) was dissolved in n-butanol (316 grams). The titanium alkoxide solution was then added to a vigorously stirred lanthanum nitrate solution (0.360 moles of La in 2L water) over 20 minutes, allowing the temperature to rise to 60°C. The Ph of the reaction mixture was maintained at 3 throughout the addition. A solution of triethanolamine (167 grams) in water (170 grams) was then added to the mixture and stirring maintained for 20 minutes at 55-60°C. This was followed by the addition of ammonia solution (320 ml, 28% w/w) over 10 minutes. The reaction mixture was allowed to cool to ambient temperature. The white precipitate formed was filtered and washed with deionised water, followed by isopropanol. The wet catalyst was dehydrated in the presence of PICOL-1095 alcohol at 100-110°C under vacuum prior to carrying out the alkoxylation reaction.

An alkoxylation process in accordance with the invention was conducted under the same general procedures described for Example 1, using as alkoxylation catalyst the hydrophobic lanthanum titanate prepared as described in this example. A total of 248 grams of NACOL-10-99 alcohol and 7.13 grams (100% actives) of hydrophobised lanthanum titanate were used. At a reaction temperature of 160°C, a total of 555 grams of ethylene oxide was taken up over a period of 65 minutes (8.5 min/mol EO). The product was analysed by GLC techniques and found to have an average adduct number of 7.5. The ethylene oxide adduct distribution of the product is presented in Figure 14.

Example 9

Self supported, hydrophobic lanthanum titanate was prepared by the following coprecipitation procedure.

Titanium alkoxide (31.6 grams of $Ti(OR)_4$ where R = ^{i}Pr (80%), R = ^{n}Bu (20%), 0.108 moles of Ti) was added to a solution of lanthanum nitrate (17.3 grams of $La(NO_3)_3.6H_2O$, 0.0400 moles of La) in ethanol (175 grams). The mixture was stirred for 2 hours and a clear Ti/La solution was obtained.

The Ti/La solution was then added to a gently stirred ammonia solution (800 ml, 3% w/w) over 75 minutes at ambient temperature. The mixture was stirred at ambient temperature for a further 60 minutes, then heated to reflux over 60 minutes. The reaction mixture was cooled, filtered and washed with water and ethanol. The wet catalyst was dehydrated in the presence of PICOL-1095 alcohol at

100-110°C under vacuum prior to carrying out the alkoxylation reaction.

An alkoxylation process in accordance with the invention was conducted under the same general procedures for Example 1, using as alkoxylation catalyst the self supported, hydrophobic lanthanum titanate prepared as described above. A total of 255 grams of PICOL-1095 alcohol and 35.0 grams of the "wet" self supported, hydrophobic lanthanum titanate (containing 18% w/w actives) were used. At a reaction temperature of 160-165°C, a total of 210 grams of ethylene oxide was added over a period of 45 minutes. The product was analysed by GLC techniques and found to have an average adduct number of 2.8. The ethylene oxide adduct distribution of the product is presented in Figure 15.

Example 9a

The self supported hydrophobic lanthanum titanate prepared and used as described in Example 9 was recovered and recycled ten times in the alkoxylation process.

The catalyst was recovered from the alkoxylation product by settling over 16 hours at 90°C followed by decantation of the supernatant alkoxylation product. The isolated catalyst was then reused in the alkoxylation process under the same procedures and conditions of Example 9. The products were analysed by GLC techniques to determine the average ethylene oxide adduct numbers and adduct distributions which are presented in Figures 16-18.

Table:
Example 9a - Recycling of Self Supported Hydrophobic Lanthanum Titanate

No. of Recycles	1	5	10
Alkoxylation Time (min/mol EO)	23	26	25
Average EO Adduct Number	3.2	3.6	3.8
EO Adduct Distribution - Figure No.	16	17	18

This example illustrates that self supported hydrophobic lanthanum titanate can be recovered and recycled whilst maintaining its activity and narrow product molecular weight distribution.

Filtration time of a sample of the self supported, hydrophobic lanthanum titanate in a C10 alcohol ethoxylate (3EO) medium was compared with filtration times of catalysts prepared as described in Examples 4 (Stage 1) and 6 under identical test conditions. This further illustrates the ease with which the self supported lanthanum titanate can be removed from alkoxylation products.

Example No	Filtration Time (min)
9	60
6	485
4, Stage 1	300

CLAIMS

1. A process for the alkoxylation of organic compounds containing at least one active hydrogen which process comprises reacting said organic compound with an alkylene oxide in the presence of a catalytically effective amount of a catalyst comprising the salt of at least one element chosen from a Group Ia or Group IIa or rare earth element and an oxy-acid of at least one element chosen from a Group IVb, Group Vb or Group VIb element or mixtures thereof wherein said catalyst is supported on an inert or active support and/or comprises hydrophobic groups.

2. A process for alkoxylation of organic compounds containing at least one active hydrogen which process comprises reacting said organic compound with an alkylene oxide in the presence of a catalytically effective amount of a supported catalyst comprising the salt of at least one element chosen from a Group Ia or Group IIa or rare earth element and an oxy-acid of at least one element chosen from a Group IVb, Group Vb or Group VIb element or mixtures thereof wherein said catalyst is supported on an inert support.

3. A process for alkoxylation of organic compounds containing at least one active hydrogen which process comprises reacting said organic compound with an alkylene oxide in the presence of a catalytically effective amount of a catalyst comprising the salt of a Group Ia or Group IIa or rare earth element and an oxy-acid of at least one element chosen from a Group IVb, Group Vb or Group VIb element or mixtures thereof wherein said catalyst comprises hydrophobic groups.

4. A process for alkoxylation of organic compounds according to any one of claims 1 to 3 wherein the catalyst component of said catalyst is selected from compounds of the general formula:

$$M_m(XO_n)$$

wherein:
M is selected from the group consisting of Li, Na, K, Mg, Ca, Sr, Ba, Sc, Y, La, Ce, Nd and mixtures thereof;
X is selected from the group consisting of Ti, Zr, Hf, Nb, Mo, W and mixtures thereof;
and m and n are selected to satisfy valency requirements.

5. A process according to claim 4 wherein n is from 2.0 to 6.0 inclusive and m is from 0.2 to 2.0 inclusive.

6. A process according to any of claims 1 to 5 wherein said catalyst component is chosen from barium titanate, barium zirconate, strontium titanate, strontium zirconate, barium strontium titanate, lanthanum titanate, potassium lanthanum titanate, yttrium titanate, lanthanum zirconate, lanthanum hafnate, barium strontium titanate zirconate, barium niobate, lanthanum molybdate, neodymium titanate and calcium titanate.

7. A process according to any of claims 1 to 5 wherein the alkylene oxide is selected from the group consisting of ethylene oxide, propylene oxide and mixtures thereof.

8. A process according to any of claims 1 to 7 wherein said organic compound is chosen from the group consisting of primary and secondary C_1 to C_{30} straight and branched chain alcohols, cycloaliphatic alcohols, glycols, polyethylene glycols, polypropylene glycols and polyhydric alcohols.

9. A process for alkoxylation of organic compounds according to any of claims 1 to 7 comprising the steps of:

adding a hydrophobic and/or supported catalyst to the organic compound containing at least one active hydrogen;

heating the reactor containing said organic compound;
supply alkylene oxide to said organic compound and hydrophobic and/or supported catalyst at a process temperature of between 50 and 250°C and at a process pressure above atmospheric pressure; and isolating the alkoxylation products.

10. A process for alkoxylation of organic compounds according to any of claims 1 to 7 claims comprising the steps of:
    adding said supported catalyst to said organic compound containing at least one active hydrogen;
    heating a reactor containing said organic compound and supported catalyst;
    supply alkylene oxide to said organic compound and supported catalyst at a process temperature of between 50 to 250°C and at a pressure above atmospheric pressure; and
    isolating the alkoxylation products.

11. A process for alkoxylation of organic compounds according to any of claims 1 to 7 comprising the steps of:
    adding a hydrophobic catalyst to said organic compound containing at least one active hydrogen;
    heating a reactor containing said organic compound and hydrophobic catalyst;
    supplying alkylene oxide to said organic compound and hydrophobic catalyst at a process temperature of between 50 to 250°C and at a pressure above atmospheric pressure; and
    isolating the alkoxylation products.

12. A process for alkoxylation of organic compounds according to any of claims 1 to 11 wherein the catalyst is recycled.

13. A process for the preparation of a hydrophobic catalyst which process comprises treating the salt of

at least one element chosen from a Group Ia or Group IIa or rare earth element and an oxy-acid of at least one element chosen from a Group IVb, Group Vb or Group VIb element or mixtures thereof with a precursor of an organic radical comprising an hydrophobic group.

14. A process for the preparation of a hydrophobic catalyst which process comprises preparing the salt of at least one element chosen from a Group Ia or Group IIa or rare earth element and an oxy-acid of at least one element chosen from a Group IVb, Group Vb or Group VIb element or mixtures thereof in the presence of a precursor of an organic radical comprising an hydrophobic group.

15. A process according to any of claims 1 to 14 inclusive wherein the level of hydrophobic and/or supported catalyst used is in the range of from 0.1 ppm to 25 percent by weight based on the weight of the organic compound containing reactive hydrogen.

16. An alkoxylation catalyst comprising the salt of at least one element chosen from a Group Ia or Group IIa or rare earth element and an oxy-acid of at least one element chosen from a Group IVb, Group Vb or Group VIb element or mixtures thereof wherein said catalyst comprises hydrophobic groups.

17. An alkoxylation catalyst comprising the salt of at least one element chosen from a Group Ia or Group IIa or rare earth element and an oxy-acid of at least one element chosen from a Group IVb, Group Vb or Group VIb element or mixtures thereof wherein said catalyst comprises hydrophobic groups and is supported on an inert or active support.

18. An alkoxylation catalyst according to claim 16 or 17 comprising compounds of the general formula I:

$$M_m(XO_n) \qquad I$$

wherein:

M is selected from the group consisting of Li, Na, K, Mg, Ca, Sr, Ba, Sc, Y, La, Ce and Nd and mixtures thereof;
X is selected from the group consisting of Ti, Zr, Hf, Nb, Mo, W and mixtures thereof;
m and n are selected to satisfy valency requirements.

19. An alkoxylation catalyst according to claim 18 wherein n has a value from 2.0 to 6.0 inclusive and m has a value from 0.2 to 2.0 inclusive.

20. An alkoxylation catalyst according to claim 18 or 19 wherein M is selected from the group consisting of K, Ca, Sr, Ba, La, Y, Nd and mixtures thereof.

21. An alkoxylation catalyst according to claim 18 or 19 wherein X is selected from the group consisting of Ti, Zr, Hf, Mo, Nb and mixtures thereof.

22. An alkoxylation catalyst according to any one of claims 16 to 18 wherein said catalyst component is chosen from barium titanate, barium zirconate, strontium titanate, strontium zirconate, barium strontium titanate, lanthanum titanate, potassium lanthanum titanate, yttrium titanate, lanthanum zirconate, lanthanum hafnate, barium strontium titanate zirconate, barium niobate, lanthanum molybdate, neodymium titanate and calcium titanate.

23. An alkoxylation catalyst according to any one of claims 16 to 22 wherein said hydrophobic groups are chosen from organic radicals containing from a C_6 to a C_{30} saturated or unsaturated, branched or unbranched, substituted or unsubstituted hydrocarbon chain.

24. An alkoxylation catalyst according to any one of claims 16 to 23 wherein said hydrophobic groups are chosen from organic radicals containing from a C_2 to a C_5 saturated or unsaturated, branched or unbranched, substituted or unsubstituted hydrocarbon chain.

25. An alkoxylation catalyst according to claim 16 or 17 wherein the catalyst is supported on an inert support chosen from the group comprising porous and non-porous alumina, silica, silica-alumina, titania, zirconia, magnesia, diatomaceous earth and similar materials, inert salts of Group IIa and rare earth elements and mixtures thereof, or polystyrene, polyethylene, polypropylene, polyimide and grafted derivatives thereof.

26. An alkoxylation catalyst according to claim 16 or 17 wherein the catalyst is supported on an active support chosen from the group comprising oxides, hydroxides or salts of Group Ia, IIa, IVb, Vb, VIb, rare earth elements or mixtures thereof, active (gamma) alumina or silica-alumina.

27. An alkoxylation catalyst according to claim 16 or 17 wherein the catalyst is supported on an active support chosen from the group comprising oxides, hydroxides and salts of Group IVb or mixtures thereof and their mixtures with the elements of Group IIIb including self supported catalysts.

28. An alkoxylation catalyst according to claims 16 or 17 the catalyst is a self-supported catalyst.

29. A supported alkoxylation catalyst according to any of claims 16 to 28 wherein the catalyst comprises from 0.5 to 100% by weight of the total supported alkoxylation catalyst.

30. A supported alkoxylation catalyst according to any of claims 16 to 28 wherein the catalyst comprises from 0.5 to 80% by weight of the total supported alkoxylation catalyst.

31. Alkoxylation catalysts substantially as herein described with reference to the Examples.

32. A process for alkoxylation of organic compounds substantially as herein described with reference to the Examples.

33. A process for preparation of a hydrophobic catalyst substantially as herein described with reference to the Examples.

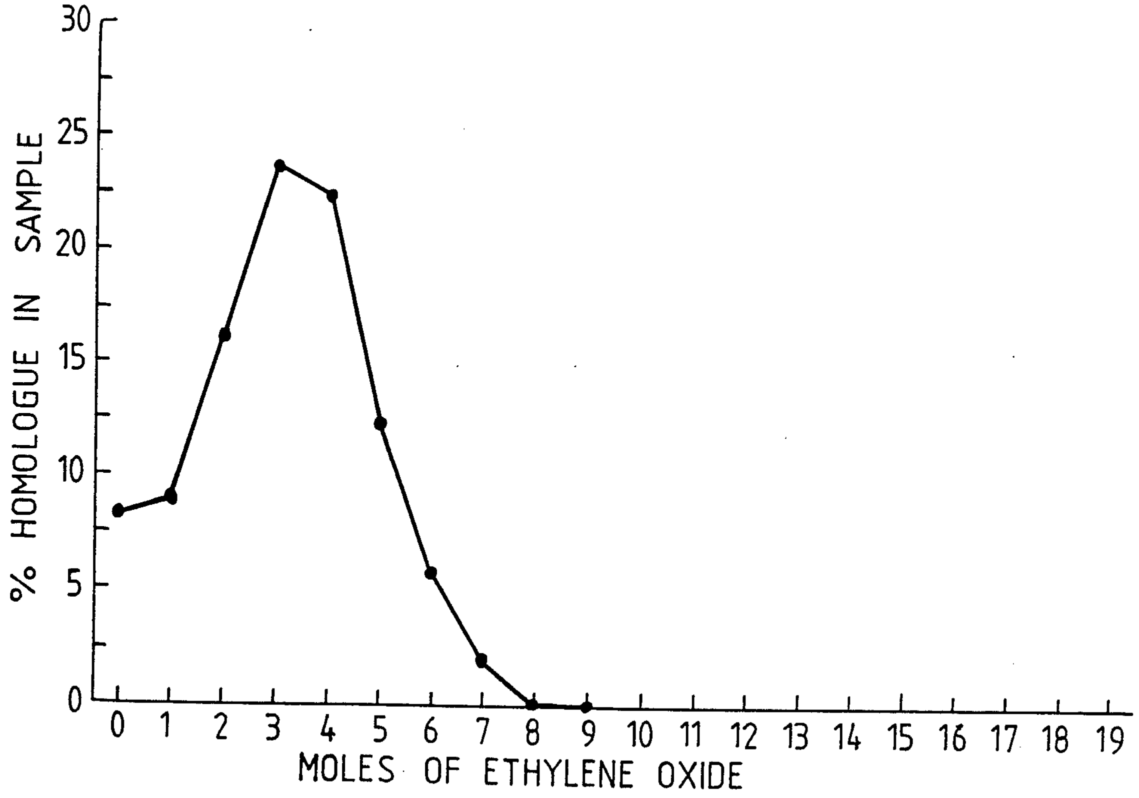
% HOMOLOGUE IN SAMPLE
30
25
20
15
10
5
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19
MOLES OF ETHYLENE OXIDE

FIG. 1.

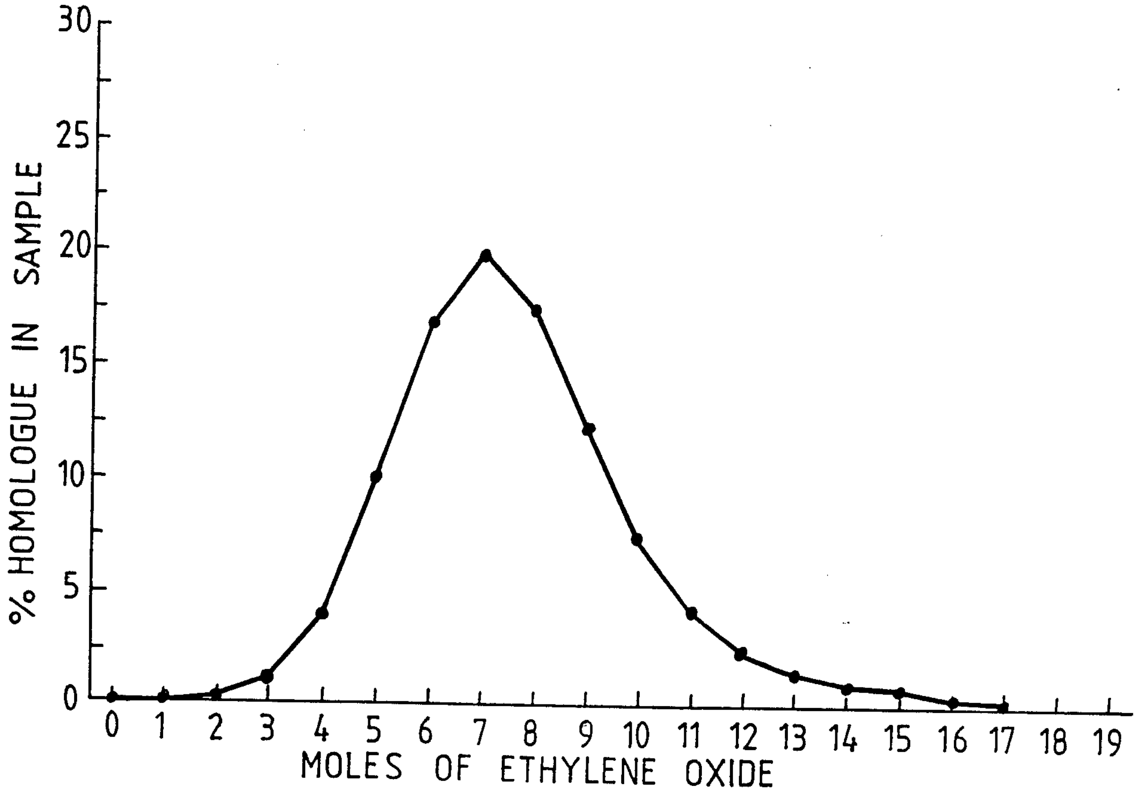
% HOMOLOGUE IN SAMPLE
30
25
20
15
10
5
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19
MOLES OF ETHYLENE OXIDE

FIG. 2.

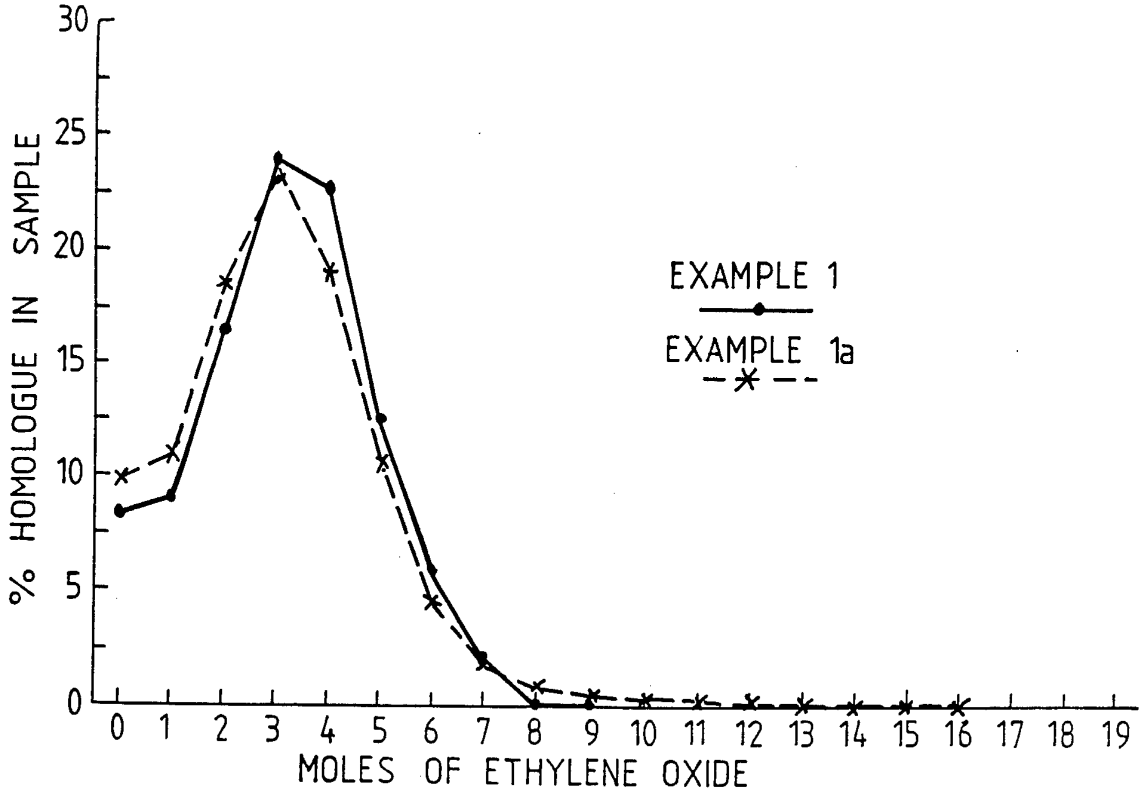
% HOMOLOGUE IN SAMPLE
30
25
20
15
10
5
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19
MOLES OF ETHYLENE OXIDE
EXAMPLE 1
EXAMPLE 1a

FIG. 3.

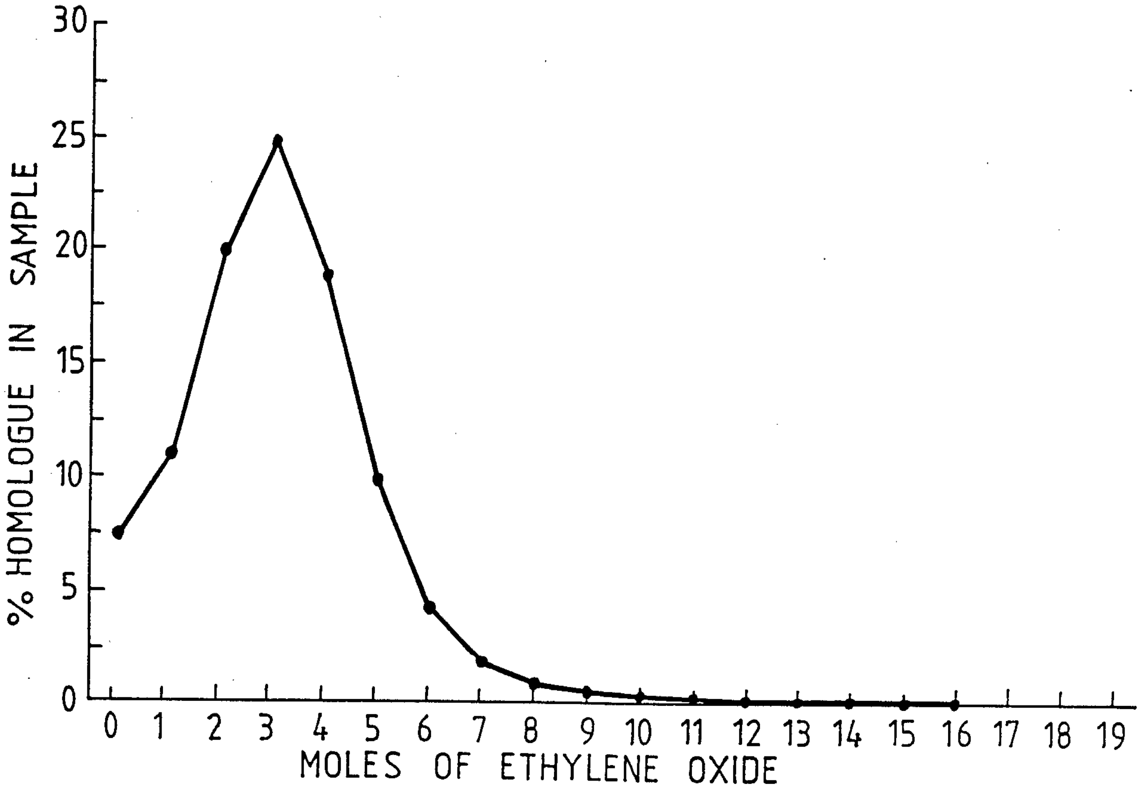
% HOMOLOGUE IN SAMPLE
30
25
20
15
10
5
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19
MOLES OF ETHYLENE OXIDE

FIG. 4.

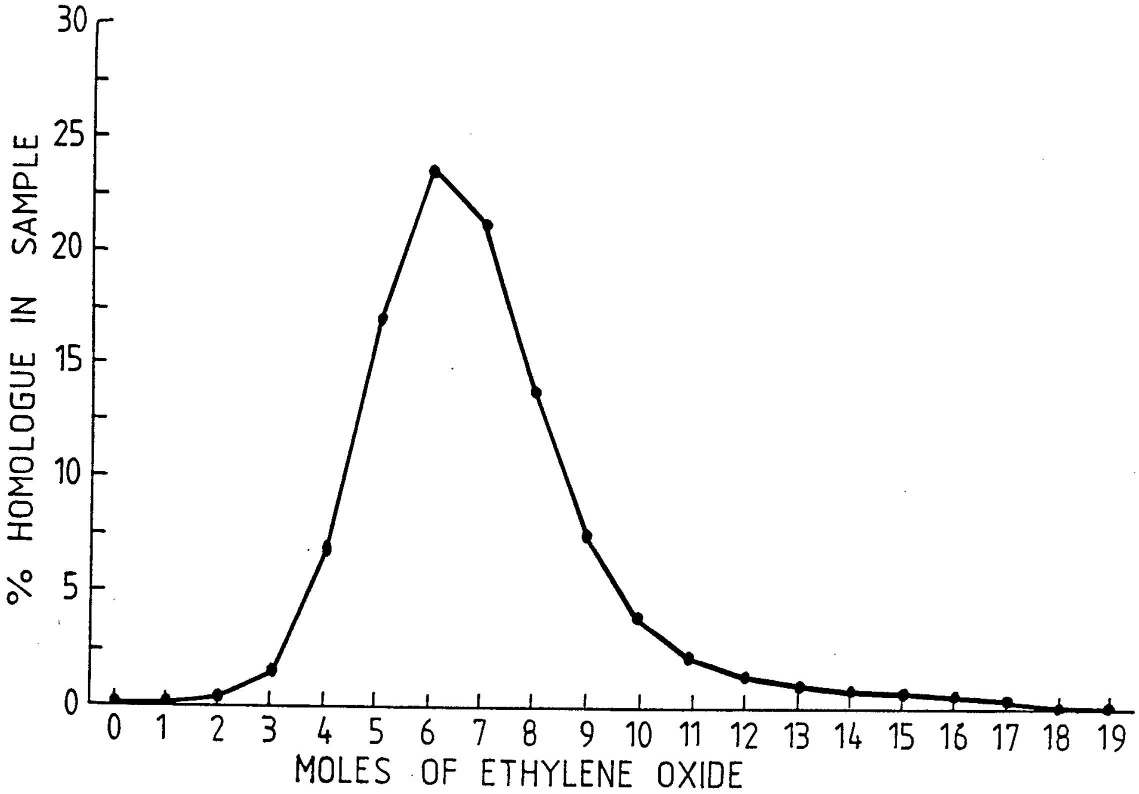
% HOMOLOGUE IN SAMPLE
30
25
20
15
10
5
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19
MOLES OF ETHYLENE OXIDE

FIG. 5.

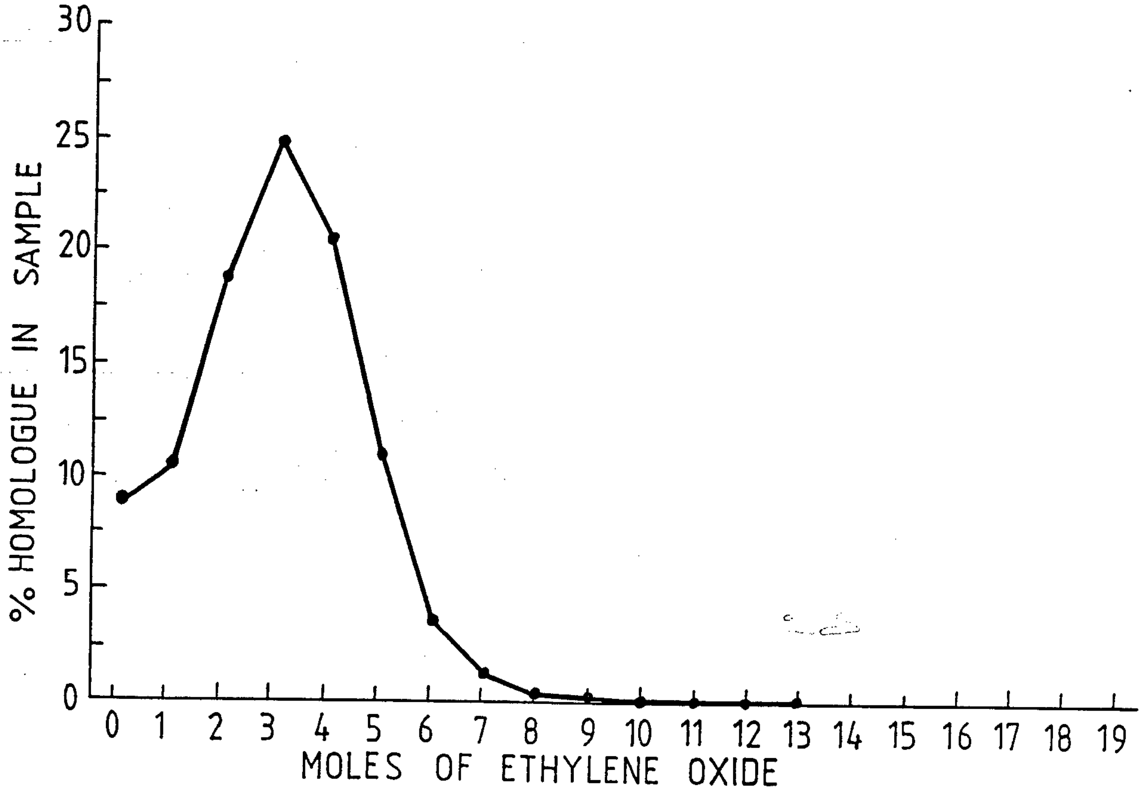
% HOMOLOGUE IN SAMPLE
30
25
20
15
10
5
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19
MOLES OF ETHYLENE OXIDE

FIG. 6.

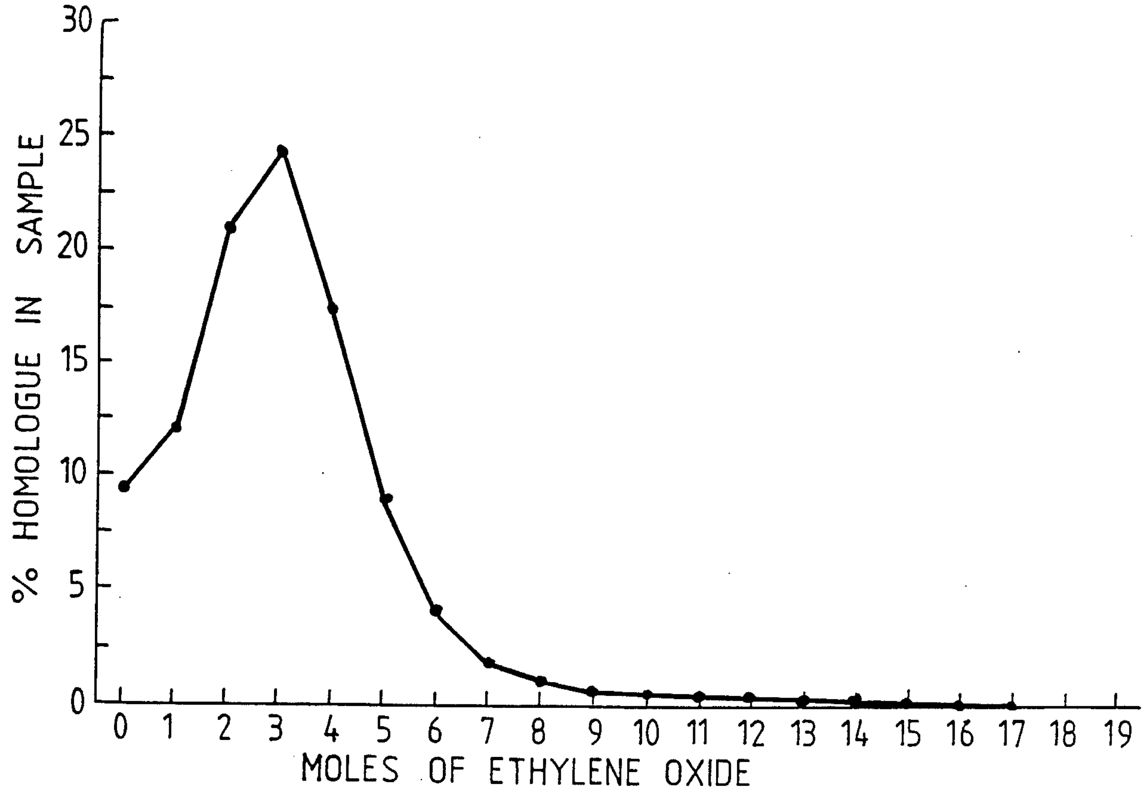
30
25
20
15
10
5
0
% HOMOLOGUE IN SAMPLE
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19
MOLES OF ETHYLENE OXIDE

FIG. 7.

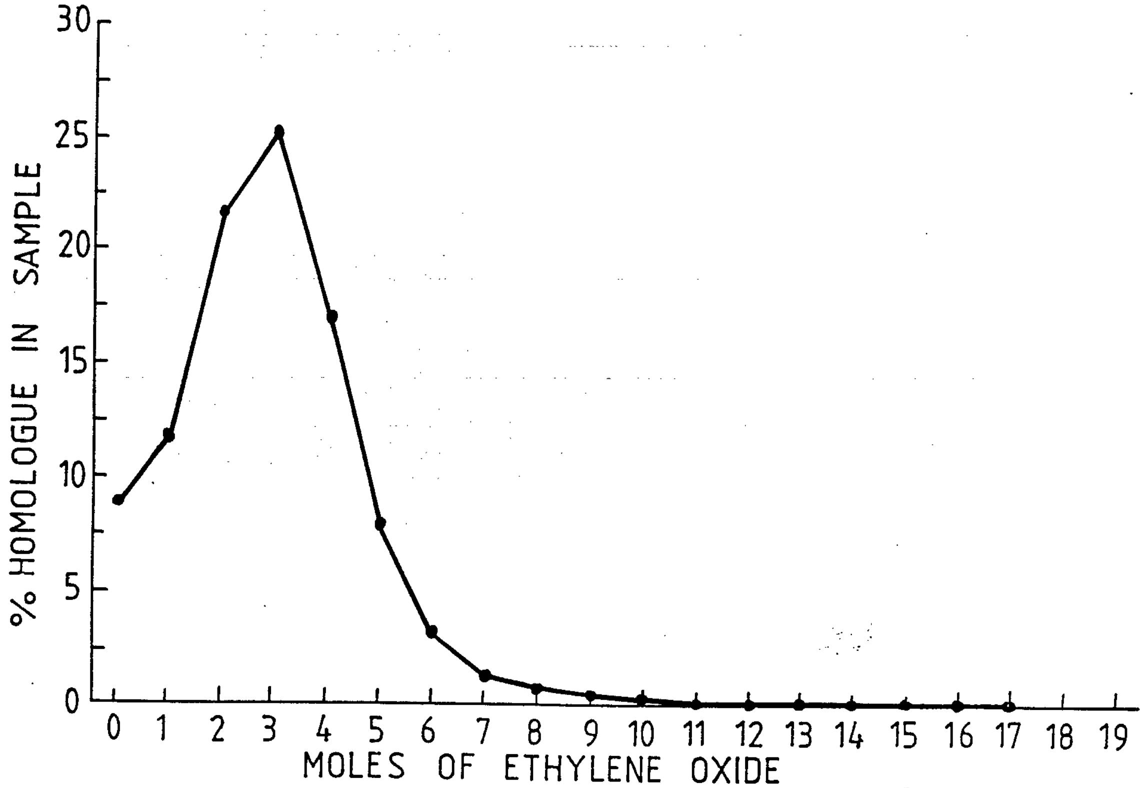
30
25
20
15
10
5
0
% HOMOLOGUE IN SAMPLE
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19
MOLES OF ETHYLENE OXIDE

FIG. 8.

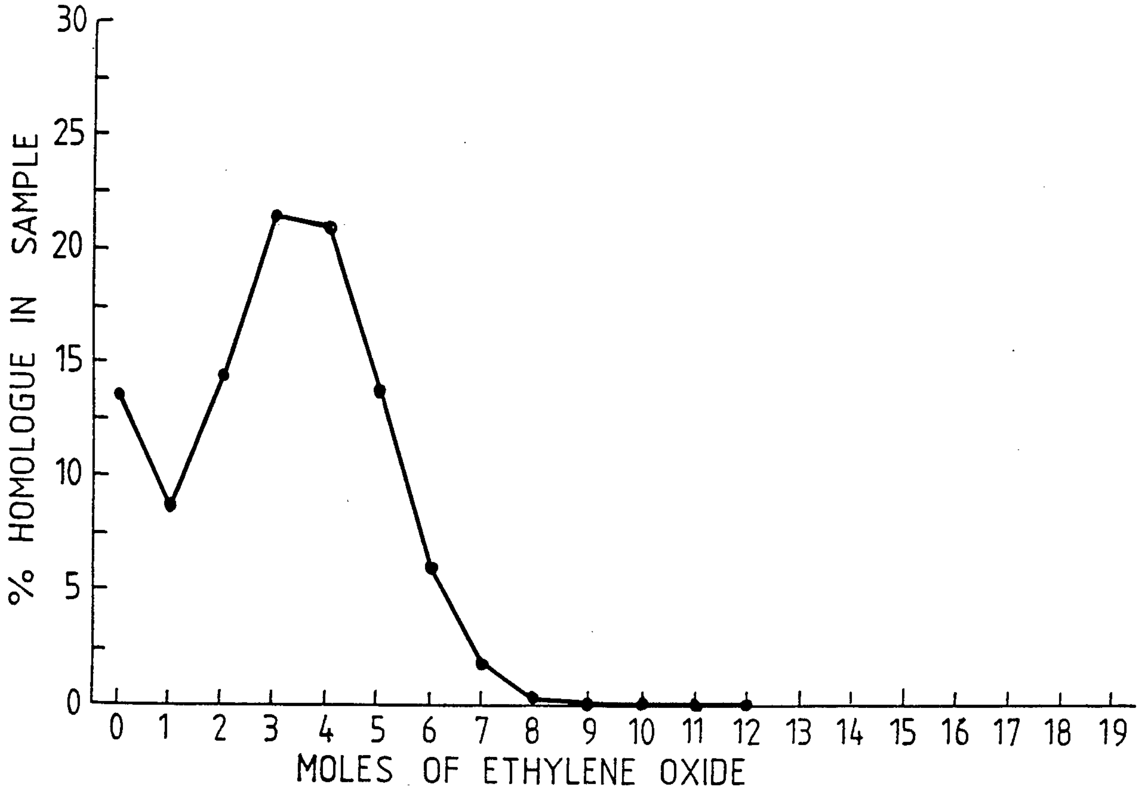
30
25
20
15
10
5
0
% HOMOLOGUE IN SAMPLE
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19
MOLES OF ETHYLENE OXIDE

FIG. 9.

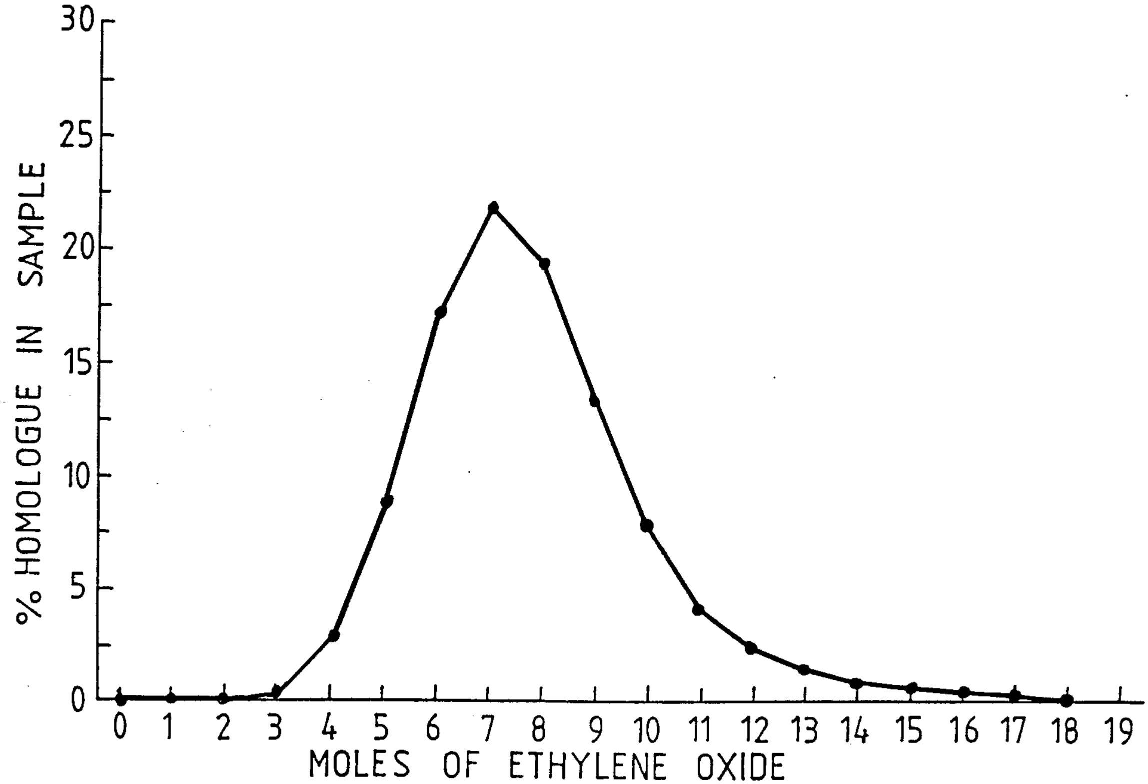
30
25
20
15
10
5
0
% HOMOLOGUE IN SAMPLE
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19
MOLES OF ETHYLENE OXIDE

FIG. 10.

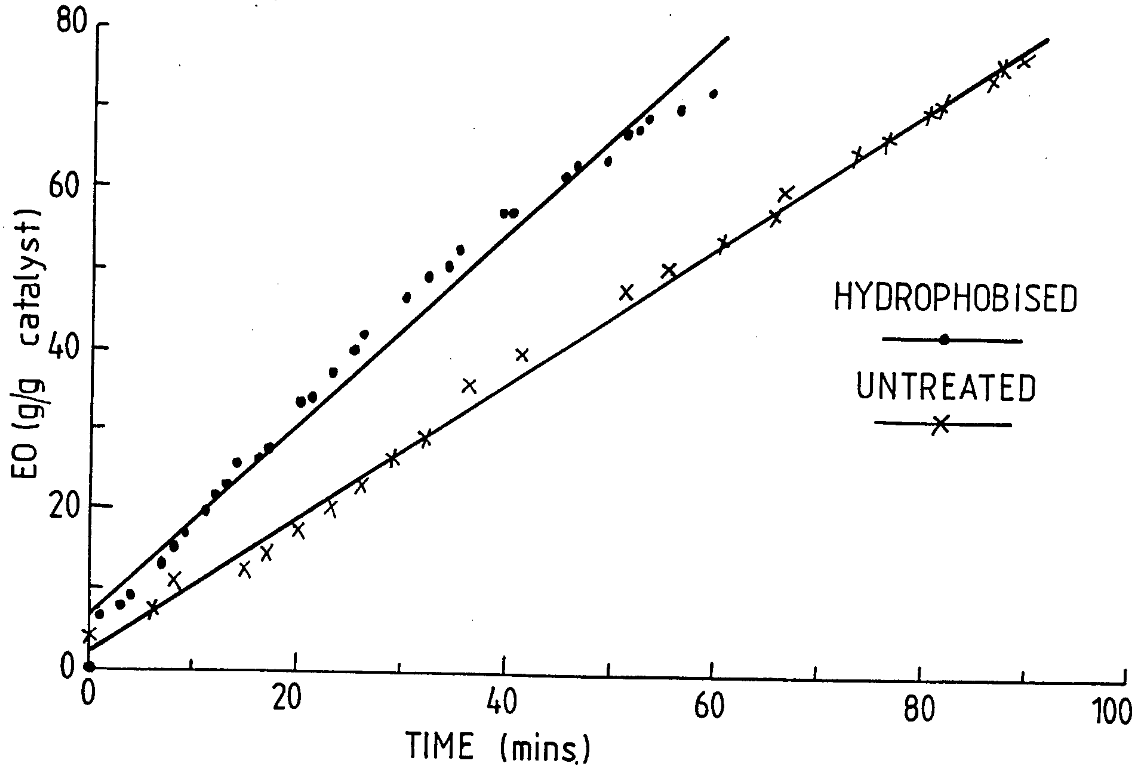
EO (g/g catalyst)
0
20
40
60
80
TIME (mins.)
0
20
40
60
80
100
HYDROPHOBISED
UNTREATED

FIG. 11.

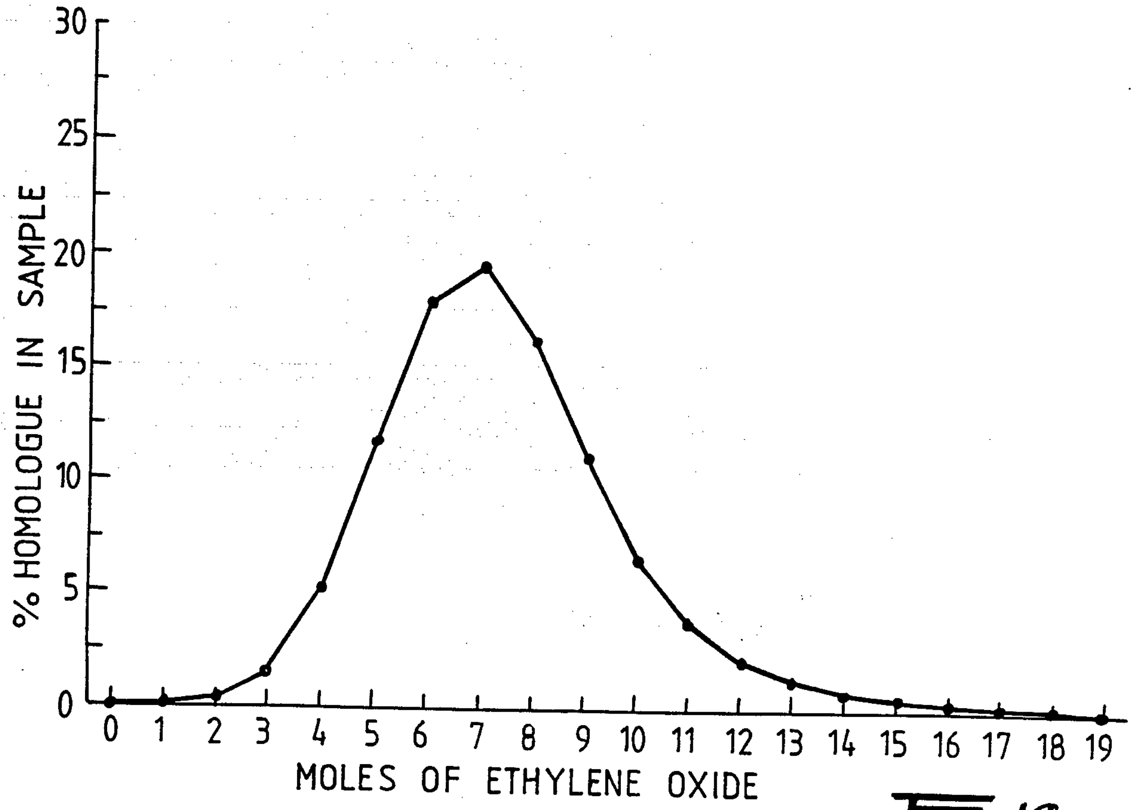
% HOMOLOGUE IN SAMPLE
0
5
10
15
20
25
30
MOLES OF ETHYLENE OXIDE
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19

FIG. 12.

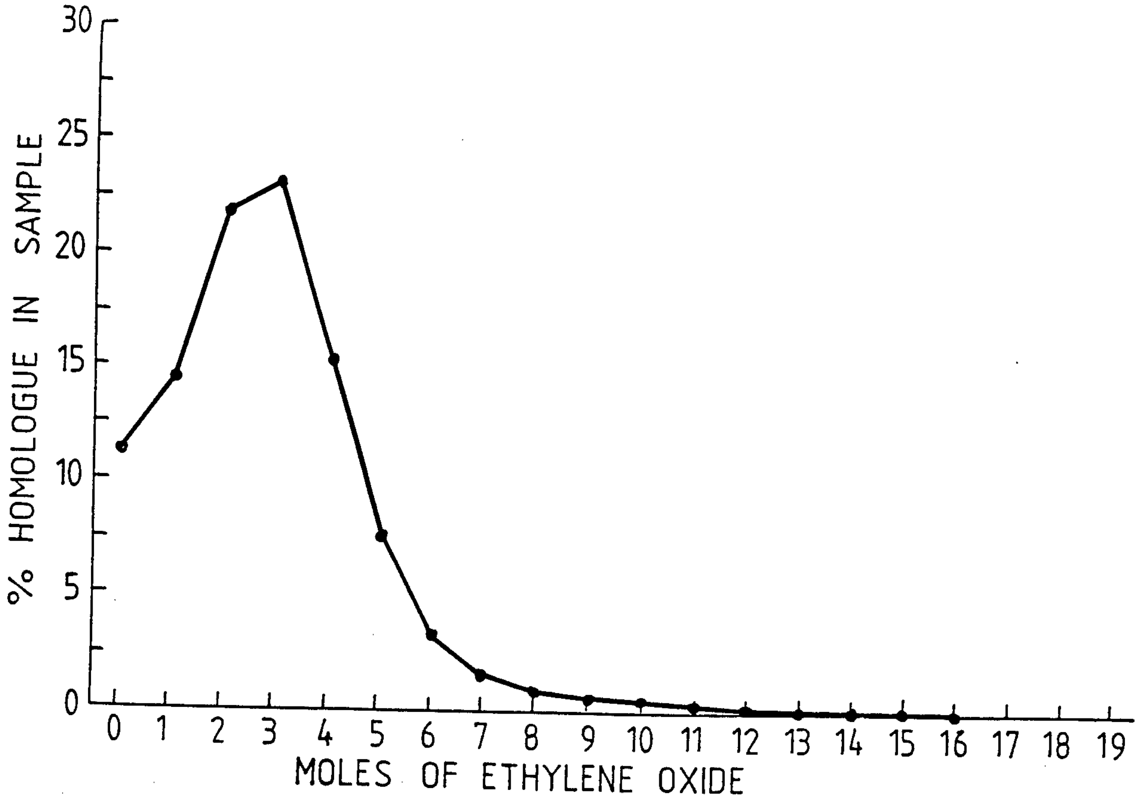
% HOMOLOGUE IN SAMPLE
0
5
10
15
20
25
30
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19
MOLES OF ETHYLENE OXIDE

FIG. 13.

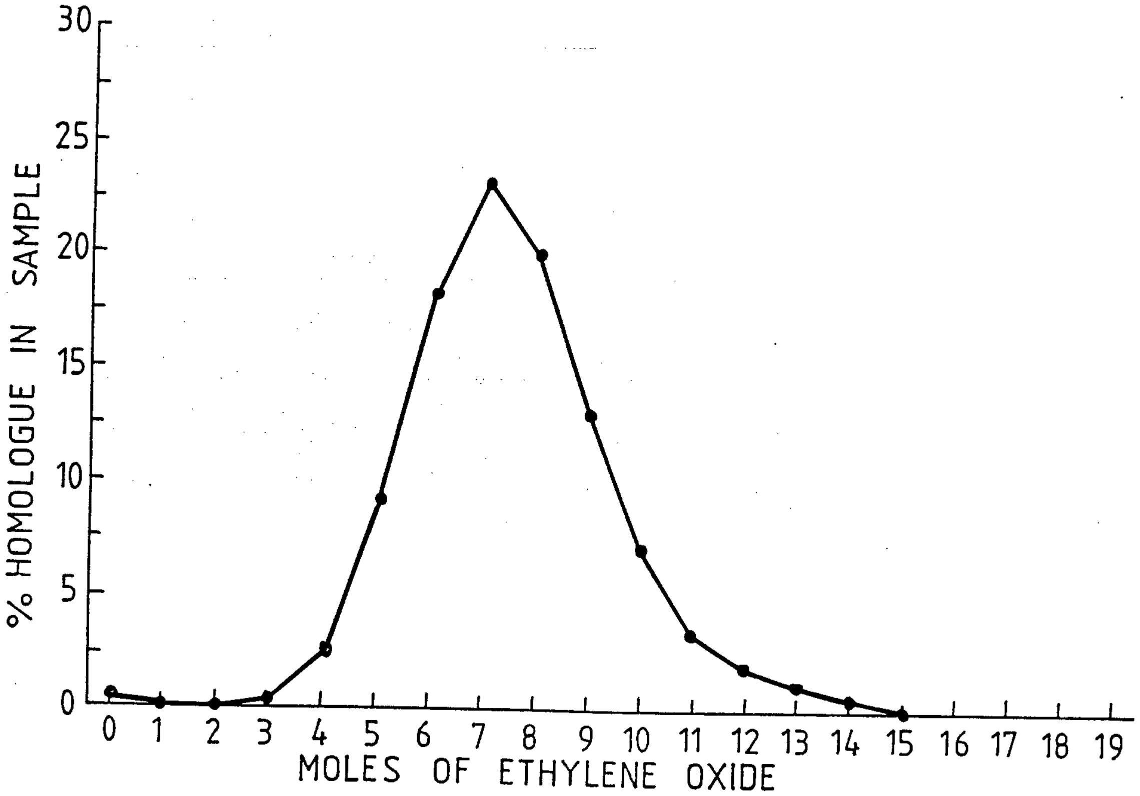
% HOMOLOGUE IN SAMPLE
0
5
10
15
20
25
30
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19
MOLES OF ETHYLENE OXIDE

FIG. 14.

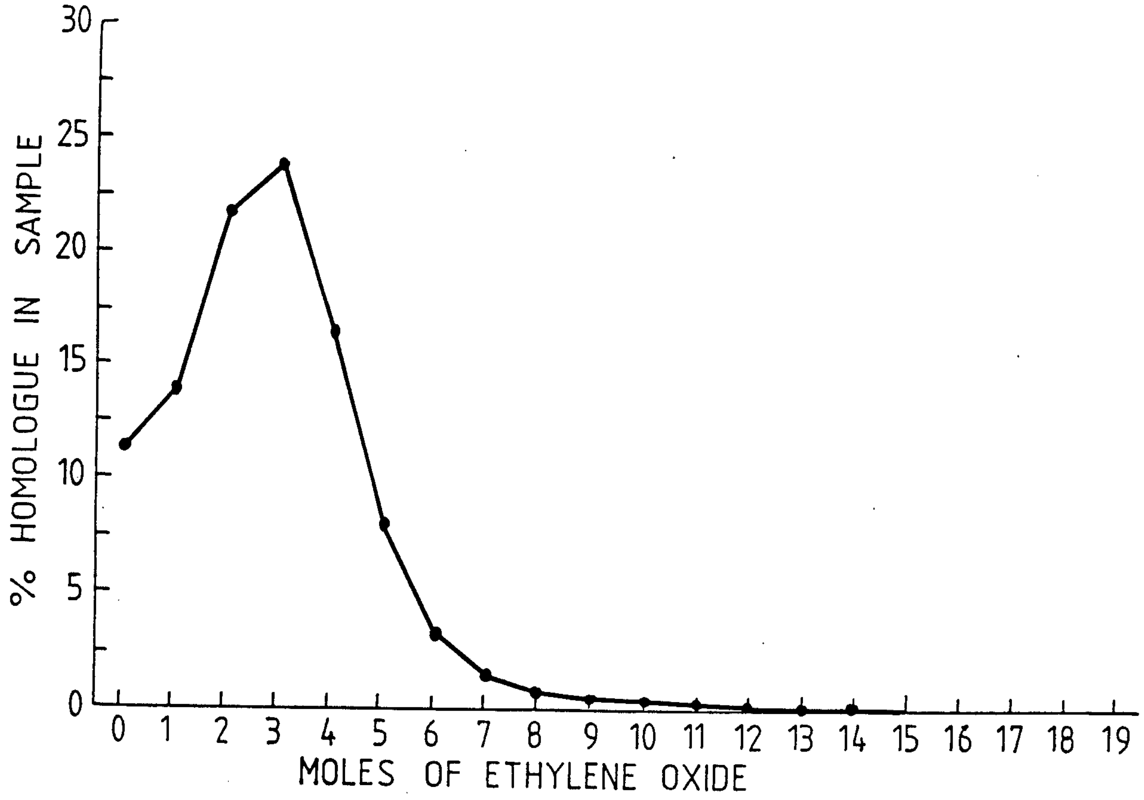
% HOMOLOGUE IN SAMPLE
30
25
20
15
10
5
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19
MOLES OF ETHYLENE OXIDE

FIG. 15.

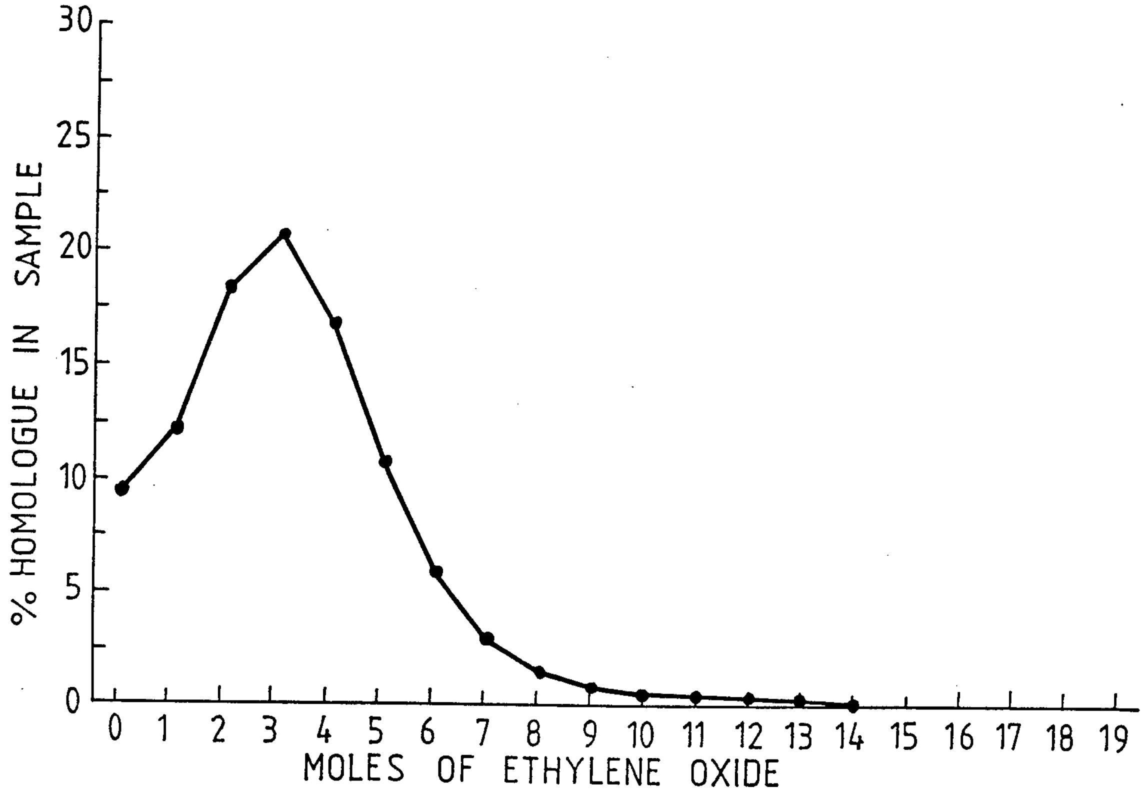
% HOMOLOGUE IN SAMPLE
30
25
20
15
10
5
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19
MOLES OF ETHYLENE OXIDE

FIG. 16.

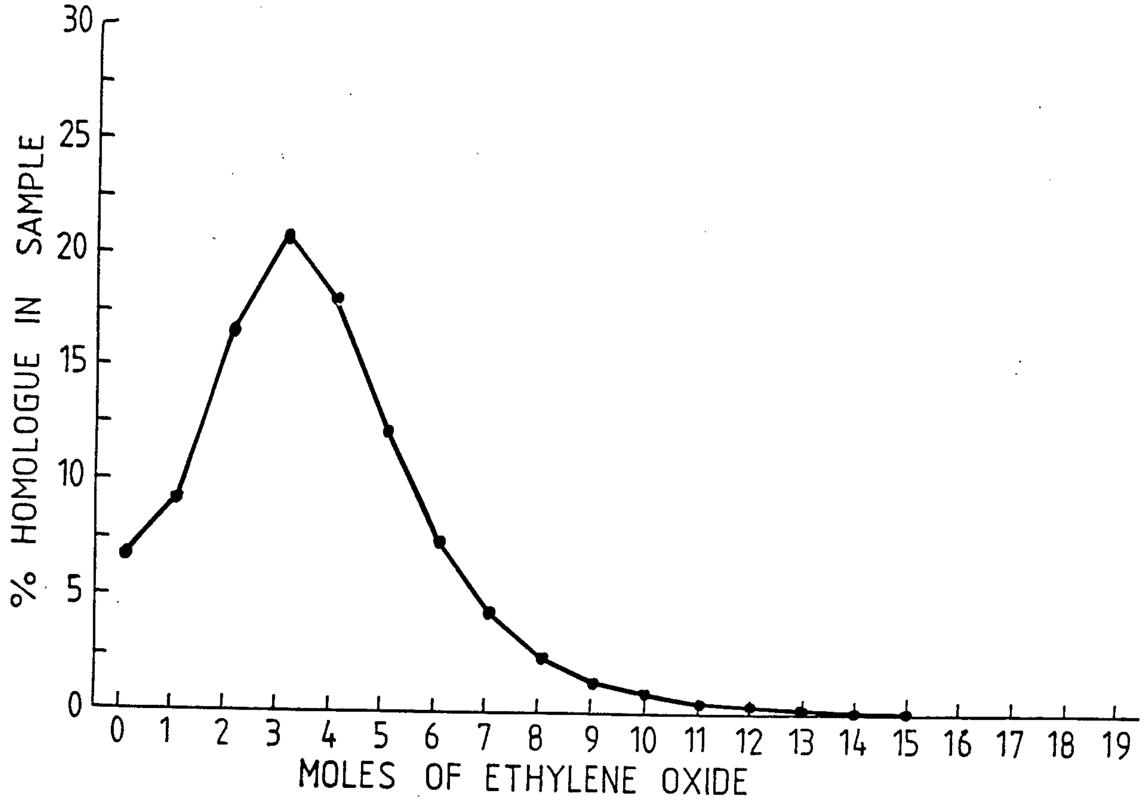
% HOMOLOGUE IN SAMPLE
30
25
20
15
10
5
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19
MOLES OF ETHYLENE OXIDE

FIG. 17.

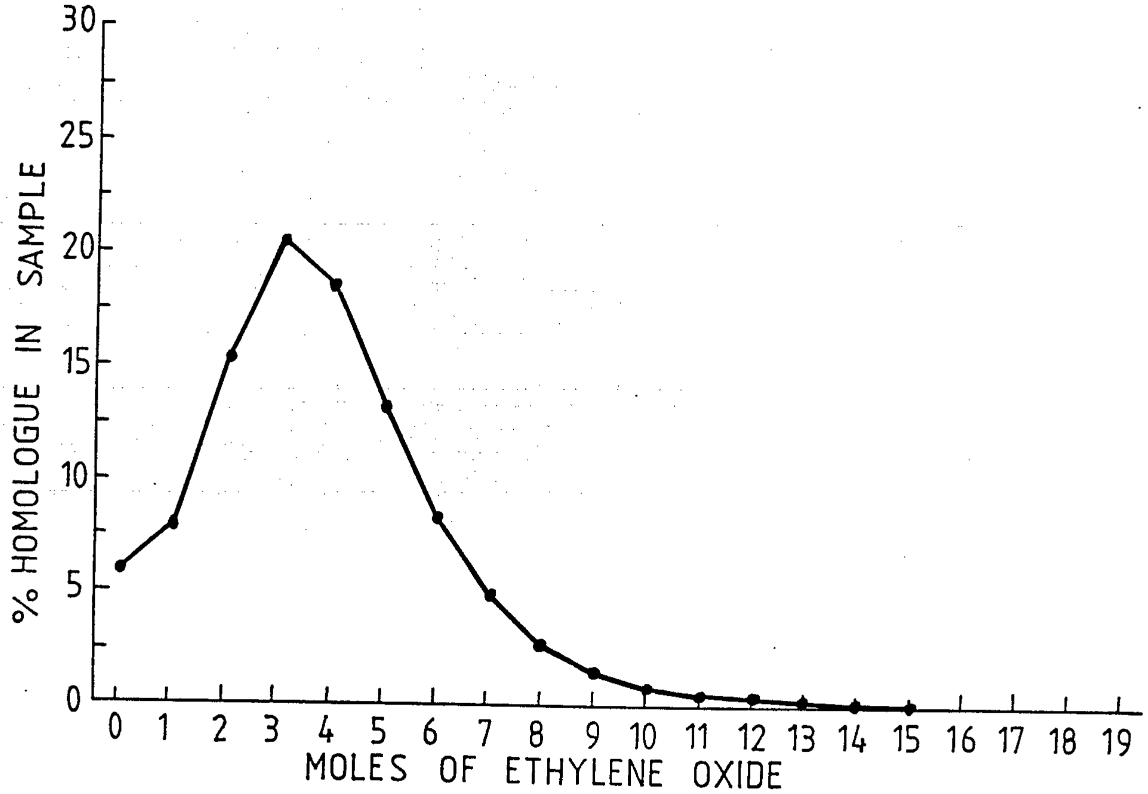
% HOMOLOGUE IN SAMPLE
30
25
20
15
10
5
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19
MOLES OF ETHYLENE OXIDE

FIG. 18.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU 94/00645

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.^{6} C07C 41/03, 43/11, B01J 31/26, 31/36, 31/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC : C07C 41/03, 43/11, B01J 31/26, 31/36, 31/38

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU : IPC as above

Electronic data base consulted during the international search (name of data base, and where practicable, search terms used)
DERWENT WPAT : (B01J 23/02, 23/04, 23/10, 23/20, 23/22, 23/24, 23/26, 23/28 or 23/30) and alkox:

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	CA,A, 1246617 (UNION CARBIDE CORPORATION) 13 December 1988 (13.12.88) See claim 1.	1
Y	US,A, 4665236 (EDWARDS) 12 May 1987 (12.05.87) See column 6 lines 17-66.	1,2
X Y	EP,A, 361616 (UNION CARBIDE CHEMICALS AND PLASTICS CO. INC.) 4 April 1990 (04.04.90) See page 9 lines 10-54, page 15 lines 39-50	1,3-33 1,2

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A"	document defining the general state of the art which is not considered to be of particular relevance
"E"	earlier document but published on or after the international filing date
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O"	document referring to an oral disclosure, use, exhibition or other means
"P"	document published prior to the international filing date but later than the priority date claimed
"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&"	document member of the same patent family

Date of the actual completion of the international search
13 January 1995 (13.01.95)

Date of mailing of the international search report
19 Jan 1995 (19.1.95)

Name and mailing address of the ISA/AU

AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION
PO BOX 200
WODEN ACT 2606
AUSTRALIA

Facsimile No. 06 2853929

Authorized officer

G. CARTER

Telephone No. (06) 2832154

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate of the relevant passages	Relevant to Claim No.
X Y	EP,A, 361617 (UNION CARBIDE CHEMICALS AND PLASTICS COMPANY INC.) 4 April 1990 (04.04.90) See page 9 lines 15-58, page 15 lines 33-44	1,3-33 1,2
X Y	EP,A, 361618 (UNION CARBIDE CHEMICALS AND PLASTICS COMPANY INC.) 4 April 1990 (04.04.90) See page 9 lines 1-58, page 14 lines 25-35.	1,3-33 1,2
X Y	EP,A, 361619 (UNION CARBIDE CHEMICALS AND PLASTICS COMPANY INC.) 4 April 1990 (04.04.90) See page 9 lines 1-47, page 15 lines 6-58.	1,3-33 1,2
X Y	EP,A, 361620 (UNION CARBIDE CHEMICALS AND PLASTICS COMPANY INC.) 4 April 1990 (04.04.90) See page 9 lines 11-53, page 15 lines 41-52.	1,3-33 1,2
X	EP,A, 387219 (JACKSON) 12 September 1990 (12.09.90) See claim 1.	16
X	EP,A, 478075 (UNION CARBIDE CHEMICALS AND PLASTICS, INC.) 1 April 1992 (01.04.92) See page 6 line 1 - page 8 line 21, claim 18.	16-33
X	EP,A, 479363 (UNION CARBIDE CHEMICALS AND PLASTICS COMPANY, INC.) 8 April 1992 (08.04.92) See page 10 line 33 - page 12 line 44.	16-33

Box I **Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)**

This international search report has not established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claim Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II **Observations where unity of invention is lacking (Continuation of item 2 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

Claim 1 in itself defines two different groups of inventions. It claims alkoxylation processes in which catalysts containing hydrophobic groups <u>or</u> a support are used. These two groups do not share a common element of novelty and are hence not so linked as to form a single inventive concept (PCT Rules 13.2 and 13.3).

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims

2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically
claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/AU 94/00645

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
CA	1246617	EP	113134	JP	59082325	US	4551566
US	4665236	CC	49052/85	CA	1260018	EP	180266
		ES	548208	ES	8701520	JP	61109746
		NZ	213962	ZA	8508199		
EP	361616	JP	2139041	US	5112788		
EP	361617	JP	2135146	US	5114900		
EP	361618	JP	2135145	US	5120697		
EP	361619	JP	2135144	US	5112789		
EP	361620	JP	2139042	US	5118650		
EP	387219	AU	49010/90	CA	2008717	EP	387219
		JP	4126550	US	5154726	CA	2007264
		EP	384906	JP	2235992	US	4895640
EP	478075	AU	84643/91	CA	2051484	JP	4279540
		MX	9101188	US	5164497		
EP	479363	AU	84637/91	CA	2051487	JP	6025051
		MX	9101183	US	5104987		
							END OF ANNEX