**Title:** HIGH CATALYST PROCESS FOR GLUCAMIDE DETERGENTS

**Abstract**

Improved process for manufacturing a linear glucamide surfactant comprising reacting an N-alkylglucamine, e.g., N-methylglucamine, a fatty ester, e.g., coconut methyl ester and a catalyst at high concentration selected from trilithium phosphate, trisodium phosphate, tripotassium phosphate, tetrasodium pyrophosphate, tetrapotassium pyrophosphate, pentasodium tripolyphosphate, pentapotassium tripolyphosphate, lithium carbonate, sodium carbonate, potassium carbonate, disodium tartrate, dipotassium tartrate, sodium potassium tartrate, trisodium citrate, tripotassium citrate, sodium basic silicates, potassium basic silicates, sodium basic aluminosilicates, potassium basic aluminosilicates and mixtures thereof.

* See back of page
+ DESIGNATIONS OF "SU"

Any designation of "SU" has effect in the Russian Federation. It is not yet known whether any such designation has effect in other States of the former Soviet Union.

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.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>AT</td>
<td>Austria</td>
<td>ES</td>
<td>Spain</td>
<td>MG</td>
<td>Madagascar</td>
</tr>
<tr>
<td>AU</td>
<td>Australia</td>
<td>FI</td>
<td>Finland</td>
<td>ML</td>
<td>Mali</td>
</tr>
<tr>
<td>BB</td>
<td>Barbados</td>
<td>FR</td>
<td>France</td>
<td>MN</td>
<td>Mongolia</td>
</tr>
<tr>
<td>BE</td>
<td>Belgium</td>
<td>GA</td>
<td>Gabon</td>
<td>MR</td>
<td>Mauritania</td>
</tr>
<tr>
<td>BF</td>
<td>Burkina Faso</td>
<td>GB</td>
<td>United Kingdom</td>
<td>MW</td>
<td>Malawi</td>
</tr>
<tr>
<td>BG</td>
<td>Bulgaria</td>
<td>GN</td>
<td>Guinea</td>
<td>NL</td>
<td>Netherlands</td>
</tr>
<tr>
<td>BJ</td>
<td>Benin</td>
<td>GR</td>
<td>Greece</td>
<td>NO</td>
<td>Norway</td>
</tr>
<tr>
<td>BR</td>
<td>Brazil</td>
<td>HU</td>
<td>Hungary</td>
<td>PL</td>
<td>Poland</td>
</tr>
<tr>
<td>CA</td>
<td>Canada</td>
<td>IT</td>
<td>Italy</td>
<td>RO</td>
<td>Romania</td>
</tr>
<tr>
<td>CF</td>
<td>Central African Republic</td>
<td>JP</td>
<td>Japan</td>
<td>SD</td>
<td>Sudan</td>
</tr>
<tr>
<td>CG</td>
<td>Congo</td>
<td>KP</td>
<td>Democratic People's Republic of Korea</td>
<td>SE</td>
<td>Sweden</td>
</tr>
<tr>
<td>CH</td>
<td>Switzerland</td>
<td>KR</td>
<td>Republic of Korea</td>
<td>SN</td>
<td>Senegal</td>
</tr>
<tr>
<td>CI</td>
<td>Côte d'Ivoire</td>
<td>LI</td>
<td>Liechtenstein</td>
<td>SU+</td>
<td>Soviet Union</td>
</tr>
<tr>
<td>CM</td>
<td>Cameroon</td>
<td>LK</td>
<td>Sri Lanka</td>
<td>TD</td>
<td>Chad</td>
</tr>
<tr>
<td>CS</td>
<td>Czechoslovakia</td>
<td>LU</td>
<td>Luxembourg</td>
<td>TG</td>
<td>Togo</td>
</tr>
<tr>
<td>DE</td>
<td>Germany</td>
<td>MC</td>
<td>Monaco</td>
<td>US</td>
<td>United States of America</td>
</tr>
</tbody>
</table>
HIGH CATALYST PROCESS FOR GLUCAMIDE DETERGENTS

TECHNICAL FIELD

This invention is in the detergent field and relates to improved processes for condensing N-alkylglucamines with fatty esters in the presence of certain catalysts to produce laundry detergent surfactant compositions.

BACKGROUND OF THE INVENTION

The present invention is set against a background of change in society's attitudes to how natural resources are used. Petroleum feedstocks are nonrenewable and increasingly costly, even impacting significantly on national balances of payment, and supply can be uncertain. There is a perception, increasingly commonly held, that it may be for the general good of society, as well as of the environment, to reduce the reliance of consumer disposable goods manufacturing on such feedstocks. However, a serious response to such notions requires efficient processes for converting locally or regionally available renewable resource feedstocks into desirable consumer goods such as laundry detergents.

The United States produces very considerable tonnages of sugars, such as glucose or corn syrup, as well as of fatty substances. There is a downward trend in traditional patterns of consumption of these particular renewable resources: people are tending to eat less sugars, and also less fatty foods, especially saturated fats, for health-related reasons. This makes their development for other uses, such as laundry detergents, all the more attractive.

A number of years ago, processes were explored for making textile assistants or detergents from fatty acids or their derivatives in combination with N-alkylglucamines, the latter made by reductive amination of glucose. Glucose reductive amination processes are more fully disclosed in U.S. Patent 2,016,962, Flint et al, issued October 8, 1935.

U.S. Patent 1,985,424, Piggott, issued December 25, 1934 discloses manufacturing "textile assistants" by reacting (a) the product of heating glucose and aqueous methylamine in presence of hydrogen and a hydrogenating catalyst under pressure with (b) an
organic carboxylic acid such as stearic acid or oleic acid. The condensation product, prepared at about 160°C, is said to be "predominantly, if not exclusively, an amide" and is assertedly of the formula R-CO-NR₁-CH₂-(CHOH)₄-CH₂OH wherein R is an alkyl radical containing at least 3 carbon atoms, while R₁ is hydrogen or an alkyl radical.

U.S. Patent 2,703,798, Schwartz, issued March 8, 1955 asserts that compositions produced by reacting fatty acids or acid anhydrides with N-alkylglucamines (presumably such as the process as taught by Piggott) have poor color and poor detergency properties. It is indeed chemically reasonable that more than one compound can be formed by the Piggott process. Piggott makes no attempt to quantitatively prove the structures of the compounds or mixtures he prepared.

Schwartz ('798) goes on to report an improvement as a result of reacting fatty ester (as distinct from fatty acid or anhydride) with N-alkylglucamines. Although this process may overcome one or another deficiency of the art, such as of Piggott, it now transpires that the Schwartz process still has difficulties, in particular, in that complex mixtures of compounds can be formed even by the Schwartz process. The reaction may take several hours and the process can fail to give high quality product. Neither the process of Piggott nor the process of Schwartz is known to have ever borne fruit in commercial practice.

In more detail, Schwartz notes that only one of several possible chemical reactions takes place when N-monoalkylglucamines are condensed with fatty esters or oils. The reaction is said to give compounds formulated as amides, e.g.,

\[
\text{O R} \\
\text{R'}-\text{C-N-CH₂(CHOH)₄-CH₂OH} \quad (I)
\]

where \( R' \) is fatty alkyl and R is a short-chain alkyl, typically methyl. This structure is apparently the same as the structure proposed by Piggott. Schwartz contrasts the single-product outcome he believes he secures with compounds he asserts are actually produced when acids are reacted with N-alkylglucamines, namely mixtures of the amide (I) with one or more by-products, to which he assigns esteramide and esteramine structures and which assertedly include compounds which are "inert and waxy, impairing the surface activity of" the structure (I) amide.
According to Schwartz, approximately equimolar proportions of N-monoalkylglucamines can be reacted with fatty alkyl esters by heating at 140°C-230°C, preferably 160°C-180°C at normal, reduced or superatmospheric pressures for a period "somewhat in excess of one hour" during which time two initially immiscible phases merge to form a product said to be a useful detergent.

Suitable N-monoalkylglucamines are illustrated by N-methylglucamine, N-ethylglucamine, N-isopropylglucamine and N-butylglucamine. Suitable fatty alkyl esters are illustrated by the product of reacting a C₆-C₃₀ fatty acid with an aliphatic alcohol e.g., methyl ester of lauric acid. Mixed glycerides of Manila oil or mixed glycerides of cochin coconut oil can apparently also be used as the fatty ester. When the glucamine is N-methylglucamine, the corresponding products with these fatty esters are characterized as the "fatty acid amides of N-methyl-glucamine", which are useful detergent surfactants. Another specific composition reported is assertedly "N-isopropylglucamine coconut fatty acid amide".

U.S. Patent 2,993,887, Zech, issued July 25, 1961 reveals there is even more complexity to the reactions of fatty substances with N-methylglucamine. In particular, Zech asserts that the products of high-temperature reaction (180°C-200°C) within the range disclosed by Schwartz have cyclic structures. No fewer than four possible structures are given. See '887 at col. 1 line 63 - col. 2 line 31.

What is now believed actually to be provided by the fatty ester- N-alkylglucamine process of Schwartz are compositions comprising mixtures of formula (I) compounds together with appreciable proportions (e.g., about 25%, often much more) of several other components, especially cyclic glucamide by-products (including but not limited to the structures proposed by Zech) or related derivatives such as esteramides wherein as compared with formula (I) at least one -OH moiety is esterified.

Moreover, a re-investigation of Schwartz suggests that there are other significant unsolved problems in the process, including a tendency to form trace materials imparting very unsatisfactory color and/or odor to the product.
More recently, the work of Schwartz notwithstanding, Hildreth has asserted that compounds of formula (I) are new. See Biochem. J., 1982, Vol. 207, pages 363-366. In any event, these compositions are given a new name: "N-D-gluco-N-methylalkanamide detergents", and the acronym "MEGA". Hildreth provides a solvent-assisted process for making the compounds differing seminally from Schwartz in that it returns to the use of a fatty acid reactant, instead of fatty ester. Moreover, Hildreth relies on pyridine/ethyl chloroformate as the solvent/activator. This process is specifically illustrated for octanoyl-N-methylglucamide ("OMEGA"), nonanoyl-N-methylglucamide ("MEGA-9") and decanoyl-N-methylglucamide ("MEGA-10"). The process is said to be cheap and high-yield. One must of course assume that "cheap" is relative and is meant in the sense of specialized biochemical applications of interest to the author: in terms of large-scale detergent manufacture, the use of pyridine and ethyl chloroformate would hardly be viewed as consistent with an economic or environmentally attractive process. Therefore, the Hildreth process is not further considered herein.

Hildreth and other workers have purified certain formula (I) compounds, e.g., by recrystallization, and have described the properties of some of the structure (I) compounds. Recrystallization is, of course, a costly and potentially hazardous (flammable solvents) step in itself, and large-scale detergent manufacture would be more economical and safer without it.

According to Schwartz supra, the products of the Schwartz process can be used for cleaning hard surfaces. According to Thomas Hedley & Co. Ltd. (now Procter & Gamble), British Patent 809,060 published February 18, 1959, formula (I) compounds are useful as a surfactant for laundry detergents such as those having granular form. Hildreth (supra) mentions use of compounds of formula (I) in the biochemistry field as a detergent agent for solubilizing plasma membranes and EP-A 285,768, published December 10, 1988 describes application of formula (I) compounds as a thickener. Thus, these compounds, or compositions containing them, can be highly desirable surfactants.

Yet another process for making compositions comprising formula (I) compounds is included in the above-identified
disclosure of improved thickeners. See EP-A 285,768. See also H. Kelkenberg, Tenside Surfactants Detergents 25 (1988) 8-13, inter alia for additional disclosures of processes for making N-alkylglucamines which, along with the above-identified art-disclosed N-alkylglucamine processes can be combined with the instant process for an overall conversion of glucose and fatty materials to useful surfactant compositions.

The relevant disclosures of EP-A 285,768 include a brief statement to the effect that "it is known that the preparation of chemical compounds of formula (I) is done by reacting fatty acids or fatty acid esters in a melt with polyhydroxy alkylamines which can be N-substituted, optionally in the presence of alkaline catalysts". The above-referenced art strongly suggests that this statement is a gross simplification or is inaccurate. EP-A 285,768 does not cite any references in support of the quoted statement, nor has any reference other than EP-A 285,768 been found which actually does disclose any catalytic condensation of N-alkylglucamines with fatty esters or fatty triglycerides.

The European Patent Application contains the following Example entitled "Preparation of N-methyl-coconut fatty acid glucamide" in which "Na methylate" is understood to be synonymous with "sodium methoxide" and which has been translated from the German:

"In a stirred flask 669 g (3.0 mol) of coconut fatty acid methyl ester and 585 g (3.0 mol) of N-methyl glucamine with the addition of 3.3 g Na methylate were gradually heated to 135°C. The methanol formed during the reaction was condensed under increasing vacuum at 100 to 15 mbar in a cooled collector. After the methanol evolution ended the reaction mixture was dissolved in 1.5 l of warm isopropanol, filtered and crystallized. After filtration and drying 882 g (=76% of theoretical) of waxy N-methyl coconut fatty acid glucamide was obtained. Softening point = 80 to 84°C; Base number: 4 mg. KOH/g."

EP-A 285,768 continues with the following:

"In a similar manner the following fatty acid glucamides were prepared:
Yield| Softening Point | Base No. |
---|---|---|
N-methyl lauric acid glucamide | 76 | 94-96 | 6 |
N-methyl myristic acid glucamide | 75 | 98-100 | 3 |
N-methyl palmitic acid glucamide | 75 | 103-105 | 5 |
N-methyl stearic acid glucamide | 84 | 96-98 | 6 |

To summarize some important points of what can be gleaned from the art, the aforementioned Schwartz patent teaches that the problem of making formula (I) compounds from fatty esters or triglycerides and an N-alkylglucamine is solved by selecting fatty ester (instead of fatty acid) as the fatty reactant, and by doing simple uncatalyzed condensations. Later literature, such as Hildreth, changes direction back to a fatty acid-type synthesis, but does not document either that the teaching of the Schwartz patent is in error or how, short of making highly pure formula (I) compounds, to make such surfactants to detergent formulator's specifications. On the other hand, there has been one disclosure, in a totally different technical field, of sodium methoxide-catalyzed formula (I) compound synthesis. As noted, the procedure involves gradual temperature staging up to 135°C and recrystallizing the product.

In view of the foregoing observations, it would be very desirable to further improve processes for making surfactant compositions comprising formula (I) compounds. Such processes should be useful on a large scale and should result directly in compositions meeting laundry detergent formulators' specifications without need for recrystallization.

Accordingly, it is an object of the instant invention to provide an improved catalyzed process for manufacturing surfactant compositions by reacting fatty esters and N-alkylglucamines in the presence of particular catalysts at elevated levels.

It is a further object to provide product compositions of the invention for use in laundry detergents, including not only linear glucamide surfactant compositions having excellent quality and color, but also compositions comprising the linear glucamide surfactant in combination with one or more solid-form alkali laundry detergent builders such as sodium carbonate.
These and other objects are secured, as will be seen from the following disclosure.

SUMMARY OF THE INVENTION

The present invention relates to an improved process for preparing detergent surfactants, more specifically, surfactant compositions having a high proportion of compounds of formula (I) wherein R' is fatty alkyl and R is a short-chain hydrocarbyl, typically methyl, ethyl or the like. Products of the invention include the detergent surfactant, as well as detergent compositions consisting essentially of mixtures of the surfactant with one or more additional laundry-useful components, especially alkaline laundry detergent builders.

In general, the process involves reacting fatty esters and N-alkylglucamines in the presence of particular catalysts at elevated levels.

Catalysts suitable for use herein are selected from the group consisting of trilithium phosphate, trisodium phosphate, tripotassium phosphate, tetrasodium pyrophosphate, tetrapotassium pyrophosphate, pentasodium tripolyphosphate, pentapotassium tripolyphosphate, lithium carbonate, sodium carbonate, potassium carbonate, disodium tartrate, dipotassium tartrate, sodium potassium tartrate, trisodium citrate, tripotassium citrate, sodium basic silicates, potassium basic silicates, sodium basic aluminosilicates, potassium basic aluminosilicates and mixtures thereof.

Most preferred catalysts include sodium carbonate, tetrasodium pyrophosphate, sodium basic aluminosilicates, sodium basic silicates and mixtures thereof.

The process efficiently converts the N-alkylglucamine, e.g., N-methyl-D-glucamine, to linear glucamide surfactant of quality suitable for the laundry detergent formulator, without need for recrystallization.

In a preferred embodiment, the invention encompasses a process wherein the catalyst is selected from the group consisting of sodium carbonate, potassium carbonate and mixtures thereof, the amount of said catalyst is from about 10 weight % to about 95 weight % based on the sum of the reactants, conversion of N-alkylglucamine to compounds having linear structure of formula
O R
\[ R' - C - N - CH_2(CHOH)_4 - CH_2OH \]
wherein R is the alkyl residue of the glucamine and R' is the residue of the fatty ester is about 70 mole % or higher on N-alkylglucamine, and conversion of N-alkylglucamine to cyclic glucamide or esteramide by-products is about 15 mole % or lower.

The present catalysts, as they operate in the process, have the advantage of not catalytically increasing the formation of by-product such as esteramide or cyclized glucamide at the same time as catalyzing the desired amidation reaction. This is surprising since esteramide by-product formation is an esterification reaction, and catalysts such as sodium carbonate or potassium carbonate have heretofore been used for catalyzing esterification reactions. See, for example, U.S. Patent 2,999,858, Curtis, issued September 12, 1961 which discloses a conversion of sucrose to sucrose fatty esters. See also U.S. Patent 3,558,597, von Brachel et al, issued January 26, 1971.

In short, the present invention is surprising in its ability to catalytically form surfactant compositions rich in formula (I) compounds selectively, without at the same time catalytically increasing by-product formation, especially by esterification.

In general, the present process takes N-alkylglucamines to linear glucamides of formula (I) with a conversion of about 70 mole % or higher, more preferably 80 mole % or higher based on N-alkylglucamine, whereas the conversion of N-alkylglucamine to by-product having cyclic glucamide or esteramide structure is generally about 15 mole % or lower.

The N-alkylglucamine starting-material can be prepared by any of the above-referenced literature methods and is illustrated by N-methylglucamine, N-ethylglucamine, N-propylglucamine and N-butylglucamine.

Highly preferred fatty ester is selected from saturated fatty methyl esters and fatty triglycerides.

The N-alkylglucamine and fatty ester are preferably used in approximately equimolar proportions in terms of the number of moles of fatty carbonyl moieties of the fatty ester per mole of N-alkylglucamine. Excellent results can also be achieved when
there is a slight excess of fatty ester, e.g., about 1.10 moles per mole of N-alkylglucamine. A slight excess of N-alkylglucamine can also be used.

The present invention has many advantages including a generally rapid and efficient process achieving a product which is useful without further purification for formulation in laundry detergents. The product of the process generally has good color and only low levels of nonvolatile by-product (notably cyclic by-product but also esteramides and the like). In certain embodiments of the invention, novel and useful compositions such as surfactant/builder intermediates for the formulator of granular laundry detergents are also secured.

Percentages and proportions herein are normally designated on a mole percentage basis unless otherwise indicated.

**DETAILED DESCRIPTION OF THE INVENTION**

The present invention relates to an improved catalyzed process for manufacturing linear glucamide surfactants from fatty esters and N-alkylglucamines. In the preferred product compositions, a high proportion (typically 70 mole % or higher, preferably 80 mole % or higher) of the N-alkylglucamine is converted to formula (I) compounds wherein R' is fatty alkyl and R is a short-chain hydrocarbyl, typically methyl, ethyl or the like.

When referring to "conversion" percentages herein, such conversion percentages are expressed on a mole percentage basis.

\[
0 \text{R}^\prime-C-N(CH_2(OH))_4-CH_2OH \tag{I}
\]

Although it is recognized that substantially pure compounds of formula (I) or, at the other extreme, highly impure compositions comprising (I) are not new, the term "linear glucamide surfactant" will be used herein to refer to the characteristic product of the process which is directly useful as a surfactant for large-scale laundry detergent formulation.

In general, "linear glucamide surfactant" as produced herein has a major proportion of the N-alkylglucamine starting-material converted to formula (I) compounds, while only minor proportions, e.g., 15 mole % or less, are converted to cyclic glucamide and/or esteramide.
By comparison, art-taught products such as those of Schwartz are believed to involve important conversion of the starting-material (e.g., 25 mole % or higher) to compounds departing from formula (I) by virtue of cyclization of the polyhydroxy moiety (cyclic glucamide) or esterification of the hydroxy moieties (esteramide).

In outline, the instant process comprises reacting a mixture of an N-alkylglucamine, a fatty ester and a catalyst, said catalyst being used at an elevated level.

Catalyst

Catalyst suitable for this invention is selected from the group consisting of trilithium phosphate, trisodium phosphate, tripotassium phosphate, tetsasodium pyrophosphate, tetrapotassium pyrophosphate, pentasodium tripolyphosphate, pentapotassium tripolyphosphate, lithium carbonate, sodium carbonate, potassium carbonate, disodium tartrate, dipotassium tartrate, sodium potassium tartrate, trisodium citrate, potassium citrate, sodium basic silicates, potassium basic silicates, sodium basic aluminosilicates, potassium basic aluminosilicates and mixtures thereof.

Preferred catalysts suitable for this invention are selected from the group consisting of trisodium phosphate, sodium carbonate, potassium carbonate, tetsasodium pyrophosphate, sodium basic aluminosilicates, sodium basic silicates and mixtures thereof.

The most highly preferred catalyst is selected from sodium carbonate, potassium carbonate, tetsasodium pyrophosphate, sodium basic aluminosilicates, sodium basic silicates and mixtures thereof.

Suitable aluminosilicates are better illustrated by the zeolites, especially Zeolite Na-A. Such siliceous catalysts are all preferably small size, such as from about 1-10 micron.

More generally, "catalyst" in the context of the present invention refers to a compound or mixture which significantly enhances the rate of formation of formula (I) compounds from N-alkylglucamine and fatty ester. This is a unique amidation reaction, since there are also present potentially reactive esterifiable or cyclizable hydroxyl groups in the N-alkylglucamine. More specifically still, the enhancement achieved by such high catalyst levels includes at the lower end of the preferred
temperatures of the process, forming the desired formula (I) compounds more rapidly than would otherwise be possible, and at the higher end of the preferred temperatures of the process, forming (I) extremely quickly, e.g., within a matter of a few minutes. Catalysts herein assist amidation without concurrently catalyzing unwanted side-reactions, such as cyclization and esteramide formation, to any appreciable extent under the reaction conditions: that is to say, the catalysts are selective.

The catalysts differ from any impurity compounds, such as water, soap or fatty acid, which might be inherent in the process when it is carried out using industrial grades of the primary reactants. Thus "catalyst" always refers to essential materials for the present process, which need to be added to the N-alkylglucamine and fatty ester for the invention to operate.

"Catalyst" is defined in a practical manner as referring to complete, stable chemical substances or mixtures thereof. The individual catalyst compounds or mixtures are available in commerce or can be made by literature methods. They can be weighed out and added to the other reactants in the instant process. Thus, catalysts herein are not defined as "active species" in the style of mechanistic discussions by chemists. Such species might or might not actually be generated in-situ in the reaction mixtures of the instant process. The invention is not to be considered limited by any such theory of catalyst operation.

Catalysts herein are generally compatible with the process. They do not contain highly reactive, grossly unsatisfactory functional groups such as peroxy, chloro, iodo, ketene, and so forth of the sort which ordinarily skilled chemists will generally recognize as not desirable for any elevated temperature amidation reactions of the present kind.

Catalysts herein preferably have particulate form: typically, they take the form of powders, as are generally available in commerce. Finely divided powders are generally preferred. Small particle sizes, such as a size of less than 50 micron or 1-10 micron can be very useful.

The preferred catalysts need not be anhydrous such as the sodium basic aluminosilicates which contain a substantial amount
of bound water. However, in the case of preferred catalysts such as tetradsodium pyrophosphate and sodium carbonate, the anhydrous form is most desirable.

Highly preferred catalysts herein generally are water-soluble or water-dispersible catalysts having monovalent cations; such preferred catalysts are more particularly illustrated by sodium carbonate, tetradsodium pyrophosphate, sodium basic silicates and sodium basic aluminosilicates.

In general, the levels of catalyst used in the instant process are of about 10 weight % or higher, e.g., from about 10 weight % to about 95 weight % based on the sum of reactants. Preferred levels are from about 25 weight % to about 85 weight %, even more preferably from about 50 weight % to about 80 weight %.

In one highly preferred embodiment of the instant process, the catalyst is anhydrous sodium carbonate powder, at a level of from about 50 weight % to about 80 weight % based on the sum of the reactants.

Mixed catalysts are also useful herein, as illustrated by mixtures of sodium carbonate and sodium basic aluminosilicates in varying proportions.

It will immediately be apparent that the instant process is remarkable in identifying much milder and more convenient catalysts than sodium methoxide for improved linear glucamide surfactant formation, which can be used at elevated levels.

**N-alkylglucamine**

Various N-alkylglucamines are useful in the practice of this invention. Such N-alkylglucamines are more specifically illustrated by N-methylglucamine, N-ethylglucamine, N-propylglucamine and N-butylglucamine. The preferred N-alkylglucamines are derived from D-glucose, e.g., N-methyl-D-glucamine.

The N-alkylglucamine can be pure or can be industrial grade provided that certain specifications are adhered to. Thus, industrial grade N-alkylglucamine may contain sugars such as glucose, sorbitol or other relatively inert by-products from N-alkylglucamine manufacture (typically 0-5 weight %). However, industrial grade N-alkylglucamines for this process should have low or negligibly small contents, in parts per million, (e.g., 0-20 ppm, preferably 0-2 ppm) of transition metals such as nickel.
if the formation of color bodies or other adverse effects are to be minimized. It has been found that industrial grade N-alkylglucamines commonly contain such transition metals as a result of their manufacture by transition metal-catalyzed reductive animation of glucose or corn syrup.

The N-alkylglucamines used herein are generally of good color, preferably pure white with no trace of colored impurities. Also, the N-alkylglucamine is preferably substantially anhydrous.

One convenient check for N-alkylglucamine quality involves simply heating a sample to the temperature of the present process, e.g., 140°C. Industrial grade N-alkylglucamines which quickly darken at such a temperature are very likely to contain unacceptable levels of impurity.

It is usually possible to clean up industrial grade N-alkylglucamines which fail initial quality checks, either by washing them with methanol/water or by recrystallizing them. A useful method for lowering the level of nickel is to filter a solution of the N-alkylglucamine through basic silica gel or bleaching earth.

Fatty Ester

The fatty ester used herein is preferably a fatty (e.g., C₁₂-C₂₀) methyl ester or triglyceride which is highly saturated, although other esters, such as saturated and mixed saturated/unsaturated fatty ethyl esters, fatty monoglycerides or fatty diglycerides can also be used. Suitable fatty esters include those illustrated by Schwartz, supra. Preferred fatty esters are better illustrated by lauric methyl ester, palmitic methyl ester or, if a mixture of chain lengths is used, coconut methyl ester. When industrial grade fatty esters are used, excellent results are achieved with the following:

Procter & Gamble CE-1270 Methyl Ester:

- Acid Value: 0.2
- Iodine Value: 0
- Moisture (% K.F): 0.03
- Color (% transmittance at 460 nm): 97
- Chain Length (GC, Wt%):
  - C 10: 0.4
  - C 12: 73.0
  - C 14: 25.9
C 16 0.2
Procter & Gamble CE-1218 Methyl Ester:
Acid Value: 0.6
Saponification Value 242
Iodine Value: 9.4
Moisture (% K.F) 0.04
Color (% transmittance at 460 nm) 97
Chain Length (GC, Wt%)

C 10 0.5
C 12 57.4
C 14 20.7
C 16 10.0
C 18 1.9
C 18 1-unsaturated 7.3
C 18 2-unsaturated 1.5
C 20 0

Substantially pure lauric methyl ester and palmitic methyl ester can of course also be used. Preferred industrial grade fatty ester for use in the present process typically contains 10 ppm or lower, better 0 ppm of heavy metals, and a free fatty acid content of 5 weight % or lower, preferably 1 weight % or lower.

The N-alkylglucamine and fatty ester mix with some difficulty in the present process. This is especially true when the fatty esters are relatively hydrophobic, e.g., the ethyl esters of C₁₆ saturated fatty acids as compared with coconut methyl esters. With the most hydrophobic fatty esters such as C₁₆ or higher ethyl esters or triglycerides, satisfactory reaction can be very difficult. To solve this problem, it has been discovered that nonionic surfactants such as a preformed formula (I) compound wherein R' is C₁₁H₂₃ and R is methyl may be used as a phase transfer agent or emulsifier. When a phase transfer agent is used in the instant process, it is used at a level of from about 0.5% to about 95% by weight of the reaction mixture, excluding catalyst. High levels such as 50% or more are best reserved for continuous mode embodiments where reaction times can be kept very short. In a batch (i.e., noncontinuous) process, a preferred level is from about 0.5 weight % to about 20 weight %, even more preferably from about 1 weight % to about 10 weight %. Such levels
are also suitable for use in continuous mode embodiments. Continuous mode embodiments will, of course, concurrently recycle some catalyst.

More generally, phase transfer agents herein comprise a member selected from the group consisting of nonionic surfactants. More preferably, the phase transfer agent consists essentially of a member selected from the group consisting of saturated fatty alcohol polyethoxylates, alkylpolyglycoside surfactants or the like.

Thus the present invention has preferred embodiments which introduce the notion of a carbonate-catalyzed, phase-transfer-assisted condensation of N-alkylglucamines and fatty esters to form surfactants of formula (I).

**Reaction Conditions**

In general, the temperatures, pressures, times and proportions of the two principal reactants can be as follows. Temperatures in the present process are normally from about 120°C to about 200°C, more preferably about 140°C or higher. Reaction periods in the process are normally from about 0.5 minutes to about 1 hour.

The invention does, however, identify preferred temperatures and reaction periods depending on whether the process is carried out in a continuous mode or a non-continuous mode. Thus, in a non-continuous mode a preferred temperature is from about 120°C to about 170°C and the corresponding reaction period is from about 5 minutes to about 60 minutes. In a continuous mode, a preferred temperature is from about 160°C to about 200°C and a corresponding period is from about 0.5 minutes to about 10 minutes. Generally, higher temperatures are accompanied by the shorter times.

Referring to the art, Schwartz favors high temperatures such as those of the order of 170°C, one must assume because he did not have suitable catalysts: such temperatures, especially with relatively long reaction times, e.g., an hour or more, can significantly increase by-product formation, especially cyclization.

EP-A 285,768 has slow heating to relatively low temperatures, specifically 135°C: this may be due to the need to avoid charring with the sodium methoxide catalyst, and is relatively uneconomic.
It is preferred to conduct the present process in the absence of air or oxygen. This is conveniently accomplished by maintaining an inert atmosphere of nitrogen or argon over the reaction mixtures, or by applying vacuum, the latter especially in the later stages of the process.

When operating uncatalyzed processes not in accordance with this invention, e.g., using the Schwartz process, at such moderate temperatures, very long reaction times (typically several hours) are required, rendering the uncatalyzed process at such temperatures rather unattractive due to long reactor hold-ups. For example, at about 150°C, the Schwartz process typically requires about 7-8 hours.

In contrast, when operating according to the present catalyzed process in the above-indicated preferred temperature ranges, e.g., at about 150°C in a batch mode at a typical catalyst level of about 30 weight %, reaction times need be no more than 20 to 30 minutes. Continuous processing with much shorter reaction times is of course possible.

According to the present invention, it is highly preferred that the reaction should be checked for completion by any suitable technique, e.g., by watching for the end of methanol evolution, by thin layer chromatography (see hereinafter), or by gas chromatography, so that it can be stopped by cooling just as soon as it is complete.

The present process is generally carried out using stirring to mix the reactants properly. It should be appreciated that at the outset of the instant process, the reaction mixtures are three-phase, the phases comprising a liquid fatty ester phase, a molten N-alkylglucamine phase and a solid catalyst phase. Therefore it can be appreciated how important it is to properly mix the reactants. Best results are generally achieved in reactors designed for effective heat and mass transfer. The use of baffles in the reactor can be advantageous.

Relative proportions of N-alkylglucamine and fatty ester are generally as disclosed by Schwartz, U.S. Patent 2,703,798, incorporated by reference. Typical proportions are approximately equimolar for best results.
Processes herein generally do not need, and are preferably conducted without added solvents and therefore generally differ from the art-disclosed process of Hildreth supra. The instant process is however tolerant of, and can even benefit from, the presence of varying amounts of methanol, ethanol, and glycerin, which are actually process by-products. Glycols such as ethylene glycol, 1,2-propylene glycol and glycerin can be added early in the process, typically in relatively small, nonsolvent amounts, as activators.

Vacuum is optionally applied during the present process, particularly as the process goes toward completion, for efficient removal of volatiles (especially methanol) when generated in the process. Use of vacuum can also improve product odor. When the fatty ester is a triglyceride, glycerin is formed during the process instead of methanol.

It is possible to use the catalyst both for its catalytic function and for other desirable functions, to have it as an integral part of the final product. Thus the process has advantages of manufacturing simplicity and is especially valuable when the catalyst is known to be useful for its laundry detergent function. What has not hitherto been appreciated is to use as catalysts for linear glucamide formation materials which can later function in the product to modify its desirable properties, such as the water-dispersability of linear glucamide-containing particles. Water-dispersibility can be modified, especially upwardly, when the catalyst or phase transfer agent is highly water-soluble, highly dispersible or capable of lowering the Krafft boundary of the glucamide. This is highly desirable for manufacture of low-temperature or all-temperature detergents.

Accordingly the new solventless approach of the present invention results in an economically attractive option for making unique granular detergent intermediates, such as particles containing intimate mixtures of linear glucamide surfactants with the catalytically active or phase transfer-active materials. Such particles are easily dispersed in water and offer increased manufacturing convenience to detergent formulators since they can be directly dry-mixed with other detergent ingredients rather than requiring additional premix process steps.
The simplicity of the present process makes it widely useful both nationally and abroad, e.g., in less sophisticated industrial economies.

The process of the invention has many alternate embodiments. Thus a number of addition sequences can be used. In one such sequence, a process is encompassed comprising the following ordered sequence of steps: (a) premixing N-alkylglucamine, the fatty ester and the catalyst to form a paste or, in the case where catalyst levels are the highest, a powdered mix results; (b) heating with mixing the paste or powder to said temperatures; (c) continuing reaction at said temperature until the end of the above-identified reaction period; and (d) cooling with stirring to form a granular product. Optionally, the product can be removed hot and allowed to cool on sheets as thin film which can be processed into granules at a later time. Another sequence involves the following steps: (a) preheating the fatty ester to the above-identified temperatures; (b) adding the N-alkylglucamine at said temperature and mixing to the extent needed to form a two-phase liquid/liquid mixture; (c) mixing in the catalyst; and (d) stirring at said temperature until the end of the above-identified reaction period.

In yet another sequence, the following steps are carried out: (a) pre-heating a solid/liquid mixture of N-alkylglucamine and fatty ester to the above-identified temperatures with mixing, thereby melting the N-alkylglucamine and concurrently mixing it with the fatty ester in the shortest practical time; (b) at said temperatures, adding pre-formed product with stirring, said pre-formed product providing linear glucamid surfactant for phase transfer and concurrently providing a portion of the catalyst; the total amount of said pre-formed product added as combined phase transfer agent and catalyst being from about 2% to about 20% by weight of the reactants excluding catalyst; (c) at said temperature, adding additional catalyst in an amount sufficient to attain the above-identified catalyst levels; and (d) continuing to react with stirring until the end of the reaction period. To such a sequence can be added a step (e): mixing the product of step (d) in molten form with further catalyst, thereby forming a linear glucamide surfactant/alkaline detergency builder mixture.
EXAMPLE I

N-methylglucamine (5.0 g., 0.0256 mole, Aldrich, AX #99922EW), methyl laurate (5.48 g., 0.0256 mole, Procter & Gamble 1295, quality code 925 605) and sodium carbonate, anhydrous powder (32.2% by weight of total reactants, 5.0 g., 0.0472 mole, J. T. Baker lot #B12172) are placed in a 50 ml beaker. The mixture is blended into a paste. The beaker is placed on a hot plate and heated. The reaction temperature is 130°C after 8 minutes. Reaction temperature is maintained between 125°C and 145°C. The beaker is removed from the hot plate after a total reaction time of 14 minutes. Analysis by TLC (see after) shows that at this point the process is complete. The final product is colorless, odorless and upon cooling has the physical form of a hard wax.

EXAMPLE II

The procedure of Example I is repeated except that an equimolar amount of methyl myristate (Aldrich lot #02022LP) is substituted for the methyl laurate. The product from the reaction upon cooling is grindable into a powder.

EXAMPLE III

N-methylglucamine (15.0 g., 0.0768 mole, Aldrich lot AX #99922EW), methyl laurate (16.46 g., 0.0768 mole, Procter & Gamble CE1295) and sodium carbonate, anhydrous powder (65.6 weight % based on the sum of reactants, 60 g., 0.571 mole, J. T. Baker lot #B12172) are combined and well mixed. The mixture has the consistency of a powder. The mixture is placed into a 250 ml stainless steel beaker and the beaker is placed into an oil bath. A motor-driven stainless steel paddle blade is used to stir the mixture. Low stirring speeds are used initially to keep the powder in the beaker. The oil bath is heated to 145°C over a 14 minute period and is maintained at this temperature. After 10 minutes the reaction mixture is a slurry which can be stirred at high speeds. Reaction is judged complete at this point by TLC. The cooled product is grindable into a powder.

EXAMPLE IV

N-methylglucamine (25 g., 0.128 mole, Aldrich lot AX99922EW) is placed in a 200 ml stainless steel beaker fitted with a motor-driven stirrer and a stainless steel stir shaft and blade. The beaker is placed into an oil bath heated at 170°C (internal
temperature typically runs from 140°C to 155°C). Coconut methylester (28.29 g., 0.128 mole, Procter & Gamble CE1270) is then added to the melted N-methylglucamine. This mixture is then heated to form a completely liquid two-phase system. Sodium silicate (31.9 weight % based on sum of reactants, 25 g., SKS-6) is then added with stirring. The reaction mixture is stirred and heated at 165°C for 30 minutes and then cooled. Reaction is judged to be complete by TLC.

EXAMPLE V

The procedure of Example IV is repeated except that sodium basic aluminosilicate is substituted for the sodium silicate and the reaction is run for 45 minutes, at which point reaction is judged complete by TLC.

EXAMPLE VI

The procedure of Example IV is repeated except that tetrasodium pyrophosphate is substituted for sodium silicate.

EXAMPLE VII

A mixture of N-methylglucamine (Aldrich M4700-0, 99%, 195 g., 1 mole) and coconut methyl ester (Procter & Gamble CE1270, 220.9 g., 1.0 mole) is melted. As soon as the melt reaches 147°C, anhydrous sodium carbonate powder (J. T. Baker 3602-01, 10.5 g., 2.5 weight %) is added. Reaction time is taken as zero. The reaction is stirred at 150°C under minimal vacuum (0-5 inches Hg vacuum) for the first 10 minutes. After a 7 minute induction period, rapid evolution of methanol occurs. Then vacuum is gradually increased with stirring at 150°C with height of foam governing level of vacuum applied. After a total elapsed reaction time of 18 minutes, a vacuum of 27 inches Hg is attained. The offwhite melt, except for 61 g. residue, is immediately blended into 1142 g. of hot (170°C) anhydrous sodium carbonate powder. A sturdy single loop beater blade attached to a high torque air drive motor is used to beat the resultant mixture. As the mixture is allowed to cool slowly (30 minutes) in ambient air, it is continuously beat vigorously. The consistency changes from initially very light to very heavy as it cools. Beating breaks it up into granules mostly less than 3 mm diameter. The granules are poured onto a tray and allowed to harden at ambient. After one hour, the product is hard enough to be bottled.
Thin Layer Chromatography (TLC) Analysis

Processes herein can be monitored by TLC using Silica Gel GF plates (Analtech) and a solvent system consisting of CHCl₃: MeOH: NH₄OH at a volume ratio of 80:23:3. Plates are preconditioned in 2:1 v/v CHCl₃:MeOH prior to use to eliminate discoloration at the solvent front.

A typical procedure for analysis involves preparing in methanol a 5-10 wt.% solution of a sample from the process. The plates are spotted with the solution, dried, and processed in the 80:23:3 solvent solution for about 10-15 minutes. Plates are removed from the processing chamber and heat-dried. Upon cooling, the plates are dipped in a 10 wt.% solution of phosphomolybdic acid and allowed to dry. The plates are then placed on hot-plate at moderate heat for 5-10 minutes until the spots are pronounced. Overheating can cause discoloration of plate and fading of spots. An iodine chamber treatment can be used instead of the phosphomolybdic acid dip but staining is less permanent. Typical RF factors are:

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>RF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unreacted N-methyl-D-glucamine</td>
<td>0.0</td>
</tr>
<tr>
<td>Fatty acid impurity</td>
<td>0.2</td>
</tr>
<tr>
<td>Formula (I) compound</td>
<td>0.3</td>
</tr>
<tr>
<td>Cyclic by-product</td>
<td></td>
</tr>
<tr>
<td>from dehydration of formula (I) compound</td>
<td>0.5</td>
</tr>
<tr>
<td>Esteramide by-product</td>
<td>0.7</td>
</tr>
<tr>
<td>Unreacted fatty ester</td>
<td>0.9</td>
</tr>
</tbody>
</table>
CLAIMS

1. An improved process for manufacturing a linear glucamide surfactant comprising reacting an N-alkylglucamine, a fatty ester, and a catalyst selected from the group consisting of trilithium phosphate, trisodium phosphate, tripotassium phosphate, tetrasodium pyrophosphate, tetrapotassium pyrophosphate, pentasodium tripolyphosphate, pentapotassium tripolyphosphate, lithium carbonate, sodium carbonate, potassium carbonate, disodium tartrate, dipotassium tartrate, sodium potassium tartrate, trisodium citrate, tripotassium citrate, sodium basic silicates, potassium basic silicates, sodium basic aluminosilicates, potassium basic aluminosilicates and mixtures thereof, said catalyst being present at levels of from 10 weight percent to 95 weight percent, based on the sum of all the reactants.

2. A process according to Claim 1 wherein said catalyst is selected from the group consisting of sodium carbonate, potassium carbonate and mixtures thereof, the amount of said catalyst is from 50 weight percent to 80 weight percent based on the sum of the reactants, conversion of N-alkylglucamine to compounds having a linear structure of formula

\[
\begin{align*}
\text{O} & \quad \text{R} \\
\text{R}' & \quad \text{C-N-CH}_2\text{(CHOH)}_4\text{-CH}_2\text{OH}
\end{align*}
\]

wherein \( R \) is the alkyl residue of the glucamine and \( R' \) is the residue of the fatty ester is 70 mole percent or higher on N-alkylglucamine, and conversion of N-alkylglucamine to cyclic glucamide or esteramide by-products is 15 mole percent or lower.

3. A process according to Claim 2 wherein said N-alkylglucamine is industrial grade N-alkylglucamine having a heavy metal content of 20 ppm or lower and a free sugar content of 5 weight percent or lower, and wherein the conversion of N-alkylglucamine to glucamide surfactant having said linear structure is 80 mole percent or higher and the conversion of N-alkylglucamine to cyclic glucamide or esteramide by-products is 10 mole percent or lower.
4. A process according to Claim 3 wherein said fatty ester is industrial grade fatty ester having a heavy metal content of 10 ppm or lower and a free fatty acid content of 5 weight percent or lower.

5. A process according to Claim 4 wherein said N-alkylglucamine, fatty ester and catalyst are reacted in a noncontinuous mode as a mixture at a temperature of from 120°C to 170°C for a period of from 5 minutes to 60 minutes.

6. A process according to Claim 5 wherein said reaction is carried out in the presence of a phase transfer agent selected from the group consisting of saturated fatty alcohol polyethoxylates, alkylpolyglycosides, linear glucamide surfactant and mixtures thereof.

7. A process according to Claim 5 comprising the following ordered sequence of steps:
   (a) preheating said fatty ester to said temperature;
   (b) adding said N-alkylglucamine at said temperature and mixing to the extent needed to form a two-phase liquid/liquid mixture;
   (c) mixing in said catalyst; and
   (d) stirring at said temperature until the end of said period.

8. A process according to Claim 6 comprising the following ordered sequence of steps:
   (a) preheating a solid/liquid mixture of said N-alkylglucamine and fatty ester to said temperature with mixing, thereby melting said N-alkylglucamine and concurrently mixing it with said fatty ester in the shortest practical time;
   (b) at said temperature, adding preformed glucamide product with stirring, said preformed product providing linear glucamide surfactant for said phase transfer and concurrently providing a portion of said catalyst; the total amount of said pre-formed product being from 2% to 20% by weight of the reactants, excluding catalyst;
(c) at said temperature, adding catalyst in an amount sufficient to attain said catalyst level; and
(d) continuing to react with stirring until the end of said period to secure the reaction product.

9. A process according to Claim 8 wherein said N-alkylglucamine, fatty ester and catalyst are reacted in a continuous mode as a mixture at a temperature of from 160°C to 200°C for a period of from 0.5 minutes to 10 minutes.

10. A process according to Claim 8 comprising the additional step of:
   (e) mixing said reaction product from step (d) in molten form with a large excess of said catalyst, thereby forming a linear glucamide surfactant/alkaline detergency builder mixture.
INTERNATIONAL SEARCH REPORT

I. CLASIFICATION OF SUBJECT MATTER
(If several classification symbols apply, indicate all)\textsuperscript{6}
According to International Patent Classification (IPC) or to both National Classification and IPC
Int.Cl. 5 C07C231/02; C07C233/18; C11D1/52

II. FIELDS SEARCHED
Minimum Documentation Searched\textsuperscript{7}

<table>
<thead>
<tr>
<th>Classification System</th>
<th>Classification Symbols</th>
</tr>
</thead>
<tbody>
<tr>
<td>Int.Cl. 5</td>
<td>C07C; C11D</td>
</tr>
</tbody>
</table>

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched\textsuperscript{9}

III. DOCUMENTS CONSIDERED TO BE RELEVANT\textsuperscript{9}

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of Document,\textsuperscript{11} with indication, where appropriate, of the relevant passages \textsuperscript{12}</th>
<th>Relevant to Claim No.\textsuperscript{13}</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>EP, A, 0 220 676 (SÜDDEUTSCHE ZUCKER-AG) 6 May 1987 see claim 2; examples A-B</td>
<td>1</td>
</tr>
<tr>
<td>A</td>
<td>WO, A, 8 304 412 (NRDC) 22 December 1983 see examples 1-6</td>
<td>1</td>
</tr>
<tr>
<td>A</td>
<td>US, A, 3 257 436 (P. LINDNER) 21 June 1966 see claim 1</td>
<td>1</td>
</tr>
</tbody>
</table>

\textsuperscript{6} Special categories of cited documents: \textsuperscript{10}

- \textsuperscript{1} document defining the general state of the art which is not considered to be of particular relevance
- \textsuperscript{E} early document but published on or after the international filing date
- \textsuperscript{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)
- \textsuperscript{O} document referring to an oral disclosure, use, exhibition or other means
- \textsuperscript{P} document published prior to the international filing date but later than the priority date claimed

- \textsuperscript{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
- \textsuperscript{X} document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
- \textsuperscript{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.
- \textsuperscript{A} document member of the same patent family

IV. CERTIFICATION
Date of the Actual Completion of the International Search
06 FEBRUARY 1992

Date of Mailing of this International Search Report
13.02.92

International Searching Authority
EUROPEAN PATENT OFFICE

Signature of Authorized Office
WELLS A.G.
This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on.
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 06/02/92

<table>
<thead>
<tr>
<th>Patent document cited in search report</th>
<th>Publication date</th>
<th>Patent family member(s)</th>
<th>Publication date</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>GB-A- 2124618</td>
<td>22-02-84</td>
</tr>
<tr>
<td>US-A-3257436</td>
<td></td>
<td>None</td>
<td></td>
</tr>
</tbody>
</table>

For more details about this annex: see Official Journal of the European Patent Office, No. 12/82