**EUROPEAN PATENT APPLICATION**

**Adhesive detergent composition**

Adhesive compositions are described, in the form of a solid, gel, or paste, cleaning and/or perfuming and/or hygienizing agents in solid, gel or paste form, which comprise i) an adhesion promoter selected from at least one amine having formula (I)

\[
\text{RN} \quad \text{R}_1 \quad (\text{C}_m\text{H}_{2m\text{O}})_x\text{H}
\]

wherein
- \(\text{R}\) and \(\text{R}_1\), the same or different, represent a linear or branched, saturated or unsaturated alkyl chain, with a number of carbon atoms varying from \(\text{C}_{12}\) to \(\text{C}_{22}\), preferably from \(\text{C}_{8}\) to \(\text{C}_{18}\), alternatively, one of the substituents \(\text{R}\) or \(\text{R}_1\) representing a \(-(\text{C}_m\text{H}_{2m\text{O}})_x\text{H}\) group;
- \(m\) varies from 2 to 4, with an alkoxylolation equal to \(x\) or \(x+y\), varying from 15 to 50 alkoxyl moles, preferably from 20 to 40, even more preferably from 25 to 35, and ii) a perfuming agent, iii) possibly a cleaning/foaming agent.

The use of said adhesive compositions in the form of a solid, gel or paste, is also described, for cleaning and/or disinfecting and/or perfuming by application onto the surface of interest of sanitary fixtures, household appliances, walls, furniture.
Description

[0001] The present invention relates to an adhesive cleaning and/or perfuming and/or hygienizing composition.

[0002] The present invention falls within the technical field of cleaning and/or perfuming and/or disinfecting products, in solid, gel or paste form, for sanitary fixtures such as interiors of WCs, bidets, pissoirs and washbasins, in particular, for the interior of dishwashers, washing machines, walls, furniture, etc., in particular the present invention falls within the technical field of products, in solid, gel or paste form, for cleaning and/or disinfecting and/or perfuming applied directly onto the surface of interest, inside sanitary fixtures or in the interior of washing machines, dishwashers, walls, furniture, to which they adhere thanks to their intrinsic characteristics, i.e. without the help of supports and/or containers, i.e. external devices.

[0003] The existence is known of adhesive cleaning and/or perfuming and/or hygienizing products, i.e. capable of adhering to the walls of the WC without the help of normal plastic cages.

[0004] The existing formulations according to the state of the art are based on the use of a group of components, ethoxylated alcohols, also defined as polyalkoxyalkanes, known as having adhesive properties. More specifically, ethoxylated alcohols are non-ionic surfactants which, in order to also have adhesive properties, must be characterized by a long hydrocarbon chain and a high ethoxylation.

[0005] Ethoxylated alcohols are prepared by the ethoxylation of alcohols, according to the following process:

\[
\text{ROH} + \text{H}_2\text{C} = \text{CH}_2 \rightarrow \text{ROC}_2\text{H}_4\text{OH}
\]

\[
\text{ROC}_2\text{H}_4\text{OH} + n\text{H}_2\text{C} = \text{CH}_2 \rightarrow \text{RO(C}_2\text{H}_4\text{O)nC}_2\text{H}_4\text{OH}
\]

[0006] Examples of hygienizing products which can be applied directly to sanitary fixtures without the help of any support and/or container based on ethoxylated alcohols can be found in EP1086199 and EP1325103.

[0007] The use of hygienizing products which can be applied directly to sanitary fixtures available on the market, however, have various drawbacks, mainly due to the specific presence of ethoxylated alcohols in the composition. When these hygienizing products, in fact, include compositions based on long-chain ethoxylated alcohols, a characteristic which, as previously indicated, is indispensable for obtaining the necessary adhesiveness, they have a low hygroscopicity.

[0008] As previously observed, in order to have a sufficient adhesiveness, ethoxylated alcohols must be alcohols with very high ethoxylation and this consequently requires that the raw material be present in solid form, in particular in the form of flakes which must be subjected to melting to form the final product, creating considerable productive difficulties. These products are therefore characterized by significant problems in the preparative phase linked specifically to the presence of ethoxylated alcohols.

[0009] The Applicant has now surprisingly found an adhesive cleaning and/or perfuming and/or hygienizing composition, in the form of a solid, gel or paste, which overcomes the drawbacks revealed by the state of the art.

[0010] The main objective of the present invention is therefore to find an adhesive cleaning and/or perfuming and/or hygienizing composition, in the form of a solid, gel or paste, which can be applied directly to the surface of interest, to which it adheres without the help of supports and/or containers, which has an optimum adhesion to the surface and duration.

[0011] A further objective of the present invention is to simplify the preparation of the adhesive cleaning and/or perfuming and/or hygienizing composition, in the form of a solid, gel or paste, which can be applied directly to the surface of interest, with a considerable reduction in the production costs.

[0012] An object of the present invention therefore relates to an adhesive cleaning and/or perfuming and/or hygienizing composition, in the form of a solid, gel or paste, characterized in that it comprises

i) an adhesion promoter selected from at least one amine having formula (I)
wherein
- $R$ and $R_1$, the same or different, represent a linear or branched, saturated or unsaturated alkyl chain, with a number of carbon atoms varying from $C_{12}$ to $C_{22}$; preferably from $C_8$ to $C_{18}$, alternatively, one of the substituents $R$ or $R_1$ represents a $-(C_{m}H_{2m}O)^{y}H$ group;
- $m$ varies from 2 to 4,
- with an alkoxylation equal to $x$ or $x+y$, varying from 15 to 50 alkoxyl moles, preferably from 20 to 40, even more preferably from 25 to 35;

ii) a perfuming agent;
iii) possibly a cleaning/foaming agent.

[0013] The alkoxy is preferably selected from ethylene oxide, propylene oxide, butylene oxide, possibly with mixed alkoxylation in random and/or block combinations.

[0014] The alkoxyated amine having formula (I) is preferably an ethoxylated amine or an ethoxylated-propoxylated amine.

[0015] The adhesive cleaning and/or perfuming and/or hygienizing composition, in the form of a solid, gel or paste, according to the present invention preferably comprises an alkanolamide selected from the compounds having formula (II)

\[
\begin{align*}
\text{R}_1 & - \text{C} - \text{N} - \text{CH}_2\text{CH}_2\text{OH} \\
\text{OR}_2 & \quad \text{X}
\end{align*}
\]

wherein
- $R_2$ represents a linear or branched, saturated or unsaturated alkyl chain, with a number of carbon atoms varying from $C_{11}$ to $C_{17}$, preferably from $C_{12}$ to $C_{16}$, even more preferably from $C_{12}$ to $C_{14}$ and $X$ is a hydrogen atom or a $\text{CH}_2\text{CH}_2\text{OH}$ group.

[0016] When $X$ is a hydrogen atom, the compound having formula (II) is a monoethanolamide, whereas when it is a $\text{CH}_2\text{CH}_2\text{O}$ group, the compound having formula (II) is a diethanolamide.

[0017] The alkanolamide having formula (II) is preferably a lauric monoethanolamide or a coconut diethanolamide.

[0018] The presence of alkanolamides allows the viscosity of the ethoxylated amine to be increased until a solid block is obtained, having adhesive properties and/or giving the composition, when necessary, cleaning and/or foaming characteristics.

[0019] The presence of detergent/foaming agents, as component (iii) of the adhesive composition according to the present invention, is envisaged for example in the case of adhesive detergents for WCs, dishwashers and washing machines, and said detergent/foaming agents can be selected from alkanolamides having formula (II), anionic- and/or non-ionic- and/or amphoteric-based surfactant mixtures (e.g. soap, sodium Laureth Sulphate, Alkylbenzensulphonate, cocoamidopropylbetaine, amine oxide etc.), and/or Syndet mixtures such as Zetasap sold by Zschimmer & Schwarz, in addition to solvent mixtures based on propylene glycol, glycerine and mixtures of sequestrants such as phosphonates, Edta, citrates, phosphates. Said detergent/foaming agents, component (iii) of the adhesive composition according to the present invention, are preferably selected from alkanolamides having formula (II).

[0020] The adhesive composition according to the present invention can also envisage the presence of viscosity
agents, such as xanthan gums, hydroxyethyl cellulose, acrylic polymers or copolymers, polyethylene glycol or polyethylene glycol distearates having a molecular weight ranging from 200 to 8,000, preferably from 1,000 to 6,000, solvents such as propylene glycol, glycerol triacetate, C₅-C₂₀ alcohols, preferably C₁₀-C₁₅, components that modify the rheology of the formulation and are suitably selected for adapting it to the distribution system and/or for vehiculating the consumption of the product.

[0021] In particular, for the synthesis of ethoxylated amines having formula (I), fatty acids (coconut and tallow are the most widely used) are adopted as precursors, which are transformed into amines and then ethoxylated, according to the following process:

\[
\text{RCO\textsubscript{H}} + \text{NH}_3 \rightarrow \text{RC\equiv N} + 2\text{H}_2\text{O}
\]

\[
\text{RC} = \text{N} + \text{H}_2 \rightarrow \text{RCH}_2\text{NH}_2
\]

In the synthesis reaction of an ethoxylated amine having formula (I) starting from a primary amine both hydrogens are substituted:

\[
\begin{align*}
\text{RNH}_2 + 2\text{C}_2\text{H}_4\text{O} & \rightarrow \text{RN} \\
\text{C}_2\text{H}_4\text{OH} & \\
\text{C}_2\text{H}_4\text{OH} & \\
\text{RN} + \text{nC}_2\text{H}_4\text{O} & \rightarrow \text{RN} \\
\text{C}_2\text{H}_4\text{OH} & \\
\text{C}_2\text{H}_4\text{OH} & \\
(\text{C}_2\text{H}_4\text{O})_x\text{H} & \\
(\text{C}_2\text{H}_4\text{O})_y\text{H} & 
\end{align*}
\]

[0022] With the above process an ethoxylated amine having formula (I) is synthesized, wherein R is a linear or branched, saturated or unsaturated alkyl chain, with a number of carbon atoms ranging from C₁₂ to C₂₂, preferably from C₈ to C₁₈, x+y is equal to n+2 and varies from 15 to 50, preferably from 20 to 40, even more preferably from 25 to 35.

[0023] In the case of an ethoxylated amine having formula (I) wherein R and R₁, the same or different, are both a linear or branched, saturated or unsaturated alkyl chain, with a number of carbon atoms ranging from C₁₂ to C₂₂, preferably from C₈ to C₁₈, the synthesis is completely analogous to that previously described for the primary amine, starting from the corresponding secondary amine. Y is not present and x, equal to n+1, varies form 15 to 50, preferably from 20 to 40, even more preferably from 25 to 35.

[0024] As previously indicated, the most widely used fatty acid precursors are coconut, which has, for example, the following composition of the alkyl chain R and/or R₁:

<table>
<thead>
<tr>
<th>Chain length</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₈</td>
<td>8</td>
</tr>
<tr>
<td>C₁₀</td>
<td>7</td>
</tr>
</tbody>
</table>
or a tallow fatty acid, which has, for example, the following composition of the alkyl chain R and/or R₁:

<table>
<thead>
<tr>
<th>Chain length</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₄</td>
<td>5</td>
</tr>
<tr>
<td>C₁₆</td>
<td>30</td>
</tr>
<tr>
<td>C₁₈ (saturated)</td>
<td>20</td>
</tr>
<tr>
<td>C₁₈ (unsaturated)</td>
<td>45</td>
</tr>
</tbody>
</table>

[0025] In the synthesis of alkoxylated amines having formula (I) according to the present invention, mixtures of the fatty acids described above can also be used as precursors.

**Formulation in gel form**

[0026] In order to obtain a good adhesion of the adhesive composition according to the present invention, in the case of formulations in gel form, the alkoxylated amine having formula (I) is present in an amount which ranges from 20% to 60% by weight with respect to the total weight of the composition, preferably from 20% to 50% and, even more preferably from 30% to 45%.

[0027] The adhesive composition in gel form according to the present invention can comprise the presence of a viscosity agent, such as for example xanthan gum, in an amount which ranges from 0% to 5% by weight with respect to the total weight of the composition, preferably from 0% to 1%, more preferably from 0% to 0.5%.

[0028] The adhesive composition in gel form according to the present invention also comprises a perfuming agent in an amount which ranges from 1% to 10% by weight with respect to the total weight of the composition, preferably from 3% to 7%.

[0029] The adhesive composition in gel form according to the present invention also comprises water in an amount which ranges from 79% to 25% by weight with respect to the total weight of the composition.

[0030] The adhesive composition in gel form according to the present invention can also comprise further components for modulating the viscosity/consistency of the gel, its duration in use, for example in a WC or inside a piece of furniture, or its melting point or again for introducing cleaning and/or foaming properties into the product, when necessary. Said further components can be selected from an alkanolamide having formula (II), anionic- and/or non-ionic- and/or amphoteric-based surfactant mixtures (e.g. soap, sodium Laureth Sulphate, Alkylbenzensulphonate, cocoamidopropylbetaine, amine oxide etc.), and/or Syndet mixtures such as Zetasap sold by Zschimmer & Schwarz, in addition to solvent mixtures based on propylene glycol, glycerine and mixtures of sequestrants such as phosphonates, Edta, citrates, phosphates, PEG, PEG distearate or a solvent such as monopropylene glycol.

[0031] The adhesive cleaning compositions in gel form according to the present invention have a viscosity ranging from 1,500 Pa·s to 5,000 Pa·s, preferably from 2,000 Pa·s to 4,000 Pa·s (measured with a Rheometrics RDAII rheometer with a plate/plate system, diameter of the plates 10 mm, shear rate 2.62 s⁻¹, temperature 20°C).

[0032] The adhesive cleaning compositions in gel form according to the state of the art based on ethoxylated alcohol are characterized by viscosity values lower than 1,500 Pa·s.

[0033] The process for obtaining an adhesive composition in gel form according to the present invention comprises the following phases.

[0034] The alkoxylated amine (preferably ethoxylated) having formula (I) is inserted in a mixer containing water at a temperature of about 40°C, and subjected to stirring until complete dissolution.

[0035] The temperature of the water can be increased if the mixing time is to be reduced, or if the percentages and/or starting components are such as to obtain a final adhesive composition having a melting point higher than 40°C.

[0036] If the adhesive composition in gel form according to the present invention comprises the addition of a viscosity agent such as xanthan gum, this must be dispersed in water before the addition of the alkoxylated amine having formula (I).

[0037] All the other components envisaged for the adhesive composition according to the present invention are then added, concluding the preparation with the addition of the perfuming agent.
Formulation in solid or paste form

[0038] In the case of formulations in solid or paste form, the amine having formula (I) is present in a quantity which varies from 20 to 76% by weight with respect to the total weight of the composition, preferably from 20 to 70%, even more preferably from 30 to 65%.

[0039] The adhesive composition in solid or paste form according to the present invention also comprises an alkanolamide having formula (II), preferably monoethanolamide or diethanolamide having formula (II), even more preferably lauric monoethanolamide, in an amount ranging from 10 to 70% by weight with respect to the total weight of the composition, preferably from 20 to 60%, to obtain a solid consistency of the formulation and/or to give cleaning properties to the product.

[0040] The adhesive composition in solid or paste form according to the present invention also comprises a perfuming agent in an amount which ranges from 1% to 10% by weight with respect to the total weight of the composition, preferably from 4 to 7%.

[0041] Alternatively, in order to obtain a solid consistency of the formulation, a particular mixture of surfactants can be used, such as soaps, lauryl ether sulfates and solvents, such as the product Zetasap C11 sold by Zschimmer & Schwarz, which in this case is a mixture of propylene glycol, soap, anionic surfactant (sodium Laureth Sulfate), sorbitol, glycerine and sequestering agents.

[0042] The adhesive composition in solid or paste form according to the present invention can comprise the presence of a viscosity agent, such as for example xanthan gum, or a solvent such as monopropylene glycol.

[0043] The process for obtaining an adhesive composition according to the present invention in solid or paste form comprises the following phases.

[0044] In a first phase, the solidifying component indispensable for obtaining the adhesive composition in solid form, such as for example lauric monoethanolamide, is melted.

[0045] The adhesion promoter, i.e. the alkoxylated amine having formula (I) is added to the molten paste thus obtained.

[0046] All the other components envisaged for the adhesive composition according to the present invention are then added, the mixing being concluded with the addition of the perfuming agent.

[0047] The adhesive composition according to the present invention can also contain, as minority components, disinfecting agents, dyes and/or cleaning adjuvants and/or foaming agents and/or cleaning agents and/or thickening agents, selected from those commonly known to experts in the field.

[0048] A further object of the present invention therefore relates to a process for the preparation of said adhesive cleaning and/or perfuming and/or hygienizing compositions in the form of a solid, gel or paste, comprising i) an adhesion promoter selected from an amine having formula (I)

\[
\text{RN} \quad \left(\text{C}_{m\text{H}_{2m}\text{O}_{x}}}H \right)
\]

(I)

wherein

- \( R \) and \( R_1 \), the same or different, represent a linear or branched, saturated or unsaturated alkyl chain, with a number of carbon atoms varying from \( \text{C}_{12} \) to \( \text{C}_{22} \), preferably from \( \text{C}_{8} \) to \( \text{C}_{18} \), alternatively, one of the substituents \( R \) or \( R_1 \) representing a \( - (\text{C}_{m\text{H}_{2m}\text{O}_{x}})_{x}H \) group;
- \( m \) varies from 2 to 4,

with an alkoxylation, equal to \( x \) or \( x+y \), varying from 15 to 50 alkoxyl moles, preferably from 20 to 40, even more preferably from 25 to 35;

- i i) a perfuming agent;
- i ii) possibly a cleaning/foaming agent,

said process comprising the following operative phases:
- heating a solidifying component, when present, for obtaining the adhesive composition in solid form, to a temperature higher than its melting point;
- incorporating component i), component iii), when present, and any further component of the composition into the melt, in any order, or directly dissolving in water, when the first phase of the process is absent, on the condition that the perfuming agent ii) is added last,
- homogenizing the composition by mixing at a temperature ranging from 35°C to 55°C for a time varying from 5 to 30 minutes,
- pouring the composition into a container,
- cooling the composition until solidification or the formation of a gel.

[0049] An object of the present invention also relates to the use of said adhesive cleaning and/or perfuming and/or hygienizing compositions in the form of a solid, gel or paste, by application onto the surface of interest of sanitary fixtures, household appliance, walls, furniture, etc.

[0050] A further object of the present invention relates to the application process of said adhesive composition directly to the surface of interest, to which it adheres without the help of supports and/or containers.

[0051] An adhesive composition in gel form according to the present invention is preferably composed of the following components:

i) ethoxylated tallow amine (C16/C18) with 25 ethoxy groups in an amount equal to 40% by weight with respect to the total weight of the composition;
ii) xanthan gum in an amount equal to 0.20% by weight with respect to the total weight of the composition;
iii) perfuming agents in an amount equal to 5% by weight with respect to the total weight of the composition;
iv) water in an amount equal to 54.80% by weight with respect to the total weight of the composition.

[0052] In another preferred embodiment, the adhesive composition in gel form according to the present invention consists of the following components:

i) ethoxylated tallow amine (C16/C18) with 25 ethoxy groups in an amount equal to 40% by weight with respect to the total weight of the composition;
ii) xanthan gum in an amount equal to 0.20% by weight with respect to the total weight of the composition;
iii) perfuming agents in an amount equal to 5% by weight with respect to the total weight of the composition;
iv) water in an amount equal to 47.80% by weight with respect to the total weight of the composition;
v) monopropylene glycol in an amount equal to 5% by weight with respect to the total weight of the composition;
vii) coconut diethanolamide in an amount equal to 2% by weight with respect to the total weight of the composition.

[0053] In further preferred embodiment, the adhesive composition in solid form according to the present invention can consist of the following components:

i) ethoxylated tallow amine (C16/C18) with 25 ethoxy groups in an amount equal to 40% by weight with respect to the total weight of the composition;
ii) lauric monoethanolamide in an amount equal to 28.80% by weight with respect to the total weight of the composition;
iii) perfuming agents in an amount equal to 4% by weight with respect to the total weight of the composition.

[0054] The main advantages of the adhesive composition according to the present invention consist in its direct applicability to the surface of interest of the sanitary fixture or interior of household appliances or furniture, its high efficacy, the modulability of its duration with time depending on the type of application, and production simplicity.

[0055] From a comparison between an ethoxylated alcohol (polyalkoxyalkane) and an ethoxylated amine, having the same chain length of carbon atoms and the same number of ethoxylations, the following different characteristics emerged.

[0056] In particular, a comparison was made between the following commercial products, compared at a concentration of 70% by weight in water:

Compound 1: EMULDAC AS 25 (ethoxylated alcohol C16-C18 ethoxylated 25 moles of EO);
Compound 2: DIAMMIN S-25 (ethoxylated tallow amine 25 moles of EO).

[0057] Firstly, as compound 1 is a solid product at room temperature, with a melting point higher than 50°C, whereas compound 2, at room temperature, is a slightly viscous liquid, the preparation process of the adhesive composition according to the present invention has definite advantages: the ethoxylated amine, in fact, does not have to be melted and can be mixed more easily with the other components of the adhesive composition according to the present invention,
such as, for example, the perfuming agent.

[0058] On the contrary, in the adhesive compositions according to the state of the art based on polyalkoxyalkanes, the polyalkoxyalkane must be melted at temperatures ranging from 50°C to 80°C to be able to be subsequently used for the production of adhesive compositions in paste form. The alkoxyalted, in particular ethoxylated, amine is, on the other hand, always in liquid form and can therefore also be used at temperatures lower than 40°C with a consequent enormous advantage from an industrial and productive point of view: the alkoxyalted amine is much easier to manage and manipulate, it requires less energy for its synthesis and its mixing with the other components of the adhesive composition is much simpler.

[0059] The insertion of the perfuming agent in the adhesive composition based on ethoxylated amine having formula (I) according to the present invention can also be effected at lower temperatures with respect to those necessary in the case of adhesive compositions based on ethoxylated alcohol, thus reducing the evaporation of the perfuming agent itself and increasing the yield.

[0060] Furthermore, an adhesive composition was tested, in gel form, according to the present invention, based on ethoxylated amine having formula (I), in particular containing compound 2 previously defined, as ethoxylated amine, i.e. ethoxylated tallow amine 25 moles of EO: this composition has a higher consistency and viscosity with respect to the adhesive composition based on ethoxylated alcohol in gel form, obtained with compound 1 according to the state of the art, and shows a greater adhesion/gluing capacity to the glass walls of a glass.

[0061] In the preparation of the adhesive compositions compared, moreover, the two solutions were heated until fluid solutions were obtained, the solution with compound 2 (DIAMMIN S-25) fluidifies at 50°C, whereas for the solution with compound 1 (EMULDAC AS-25) a further 10°C approximately are necessary for obtaining a fluid solution: consequently the significant productive advantage linked to the use of alkoxyalted amine, in particular ethoxylated, having formula (I) as adhesion promoters for producing an adhesive cleaning and/or perfuming and/or hygienizing composition, in the form of a gel, paste or solid, is yet again evident. The two solutions thus obtained were then cooled slowly; they return to forming a gel phase: the solution with compound 2 (DIAMMIN S-25) again formed the initial gel, whereas the solution with compound 1 (EMULDAC AS-25) tends to solidify on the surface or upper part of the solution, consequently not uniformly: this shows that the alkoxyalted amine (in particular ethoxylated) having formula (I) allows stable pastes to be obtained, which, even when subjected to thermal stress such as that caused by the transportation of the product during its commercialization or industrial moving, maintain their physico-chemical properties. The solutions based on ethoxylated alcohols or polyalkoxyalkanes according to the state of the art, are, on the other hand, much more subject to physical modifications due to sudden temperature changes.

[0062] This is due to the fact that polyalkoxyalkanes increase their miscibility in water with an increase in temperature, but an aqueous solution containing polyalkoxyalkanes, after heating, can lead to separation into a phase rich in surfactant and a phase poor in surfactant. This effect is absolutely less marked in the case of solutions based on ethoxylated amines which, thanks to their partial cationic nature, are capable of ionizing in water maintaining a stable solution.

[0063] In order to overcome the above drawback and obtain a more stable gel, in the case of polyalkoxyalkane surfactants, it is necessary to increase the ethoxylation. This increase however could lead to producing products in flakes, hence to significantly also increasing the melting point of the polyalkoxyalkane, thus further aggravating the problems previously indicated, linked to the lower yield of the perfuming agent and more difficult industrialization of the adhesive composition.

[0064] In the adhesive compositions according to the present invention, the alkoxyalted amines, in particular ethoxylated, having formula (I) have a high foaming capacity, whereas ethoxylated alcohols produce a moderate foam; they are in fact used for minimizing the foam of anionic surfactants: in adhesive cleaning compositions such as adhesive compositions in paste form for WCs, the foam, together with the perfume, is a characteristic of fundamental importance for obtaining a particularly effective adhesive composition.

[0065] It is therefore evident that, in the case of the use of ethoxylated alcohols as adhesion promoters, the adhesive composition will require an anionic surfactant as foaming agent, but the amount of foam it produces will in any case be minimized by the presence of the same ethoxylated alcohol.

[0066] In the case of the adhesive compositions according to the present invention, only one ethoxylated amine can be used together with the perfuming agent, obtaining an adhesive composition in the form of a paste with adhesive perfuming properties and which produces a good quantity of foam.

[0067] In the adhesive compositions according to the present invention, the alkoxyalted amines, in particular ethoxylated, having formula (I) also have another characteristic of particular interest: they have proved to be extremely hydroscopic, this means that they easily absorb water, favouring the dissolution of the adhesive composition in paste or solid form during use, for example in WCs where, during the flushing of the water, part of the cleaning, perfuming and/or hygienizing composition must dissolve to exert its specific activities of an adhesive composition of this type (foam, perfume and detergent).

[0068] The alkoxyalted, in particular ethoxylated, amine having formula (I) present in the adhesive composition according to the present invention facilitates dissolution, whereas in the adhesive compositions based on ethoxylated
alcohols according to the state of the art, as the ethoxylated alcohol has lower hygroscopic properties, the dissolution of the adhesive composition must be helped by the insertion in the formula of humectants such as polyethylene glycols or other solvents: the presence of these components can negatively influence two of the three fundamental characteristics of a cleaning composition in general, i.e. the perfume and the foam. Solvents are in fact the source of additional strong odours which conceal the perfume and are foam demolishers. The presence of alkoxylated amines having formula (I) in the adhesive compositions according to the present invention allows cases in which it is necessary to insert humectants and/or solvents in the formulation to be reduced to the minimum and in these cases however, to add an extremely limited quantity of said components.

Definite advantages are also linked to the hygroscopicity of the alkoxylated, in particular ethoxylated, amine having formula (I), in the case of adhesive compositions in gel form, but also in adhesive compositions in the form of a solid or paste: an adhesive composition based on alkoxylated amine, in particular ethoxylated amine, having formula (I), as adhesion promoter, also comprising a component having a solidifying action, such as an alkanolamide having formula (II) and in particular a lauric monoethanolamide or another solidifying and/or cleaning agent, can in fact be easily produced in the form of a solid block having adhesive properties. The solid can be enclosed in a plastic container without particular problems of detachment of the adhesive composition from the container during the application of the adhesive composition to the surface of interest.

In fact, the hygroscopicity of the alkoxylated, in particular ethoxylated, amine allows the formation of a light layer of hydrated, and therefore liquid, ethoxylated amine to be obtained between the surface of the plastic container and the solid block, and this layer of hydrated ethoxylated amine acts as detaching agent of the solid block from the support.

The production of a solid block with an adhesion promoter consisting of ethoxylated alcohol, due to the adhesive properties of the same and lack of hygroscopicity, leads to obtain a solid adhesive composition in which the detachment of the solid block from the plastic carrier for the utilization of the detergent product, is almost impossible.

The adhesive cleaning and/or perfuming and/or hygienizing composition in solid, gel or paste form, according to the present invention, i.e. based on alkoxylated amine (preferably ethoxylated) having formula (I), capable, as a result of its intrinsic characteristics, of adhering to sides, such as the inside of WCs, the interior of dishwashers, walls, etc., i.e. without the help of an external device, therefore has the following advantages both as final benefits for the user, and also from a productive/industrial point of view, with respect to adhesive compositions based on polyalkoxyalkanes as adhesion promoters according to the state of the art:

- adhesive composition with higher perfuming performances, due to a production process which allows the loss, by evaporation, of the perfume introduced into the formula, to be reduced,
- adhesive composition less sensitive to thermal stress, maintaining its physico-chemical characteristics unaltered even when subjected to sudden temperature changes,
- adhesive composition performing with a lower number of components and consequent ecological and economical advantages, on both a production level, and also for the final user,
- adhesive composition more versatile for the production of different solid or gel forms of the product,
- liquid raw material easier to manage,
- less energy required for the production.

Furthermore, with respect to preparation processes of analogous hygienizing products, there are also the following advantages of the process object of the present invention:

- the solidified end-product does not require mechanical finishing treatment (e.g. drawing);
- the heating of the composition is extremely limited (at the most to reaching the melting point of the solidifying component such as alkanolamide); this avoids the evaporation of volatile substances such as perfuming agents;
- the composition is poured into and solidified in a container which confers the final form of the product ready for use and does not require further processing (e.g. line-end cutting);
- end-products having numerous forms can be obtained, unlike traditional drawing-extrusion processes which strongly limit the variety of possible configurations.

The adhesive composition in solid form according to the present invention can be produced in the form of a tablet having dimensions of about 4 x 2 x 1 cm, making it only slightly visible inside the surface of interest to which it is applied, unlike the much more encumbering products which can be obtained according to the disclosures of the state of the art.

The encumbrance of the adhesive composition according to the present invention mainly depends on the duration of the hygienizing efficacy to be obtained.

If, for the hygienizing of a household WC, an adhesive composition is considered to be subjected to flushings of discharge water varying from 6 to 9 litres each, the adhesive composition according to the present invention formulated
as a tablet having a weight of about 10 grams, is completely washed away only after 90-130 flushings approximately, bearing in mind that the number of flushings necessary for the complete washing away also depends on the geometry of the tablet and flushing mode of the water in the WC.

The use of the adhesive composition according to the present invention for cleaning and/or disinfecting and/or perfuming sanitary fixtures occurs through the direct application to the sanitary fixture, to which it adheres without the help of supports and/or containers.

In particular, in order to facilitate the application of the composition to the sanitary fixture, the composition can be provided with a support, such as for example a plastic thermoformed support from which the adhesive composition can be easily detached thanks to the hygroscopic characteristics described above, of the alkoxylated amine itself.

The following examples are provided for purely illustrative purposes.

Examples 1-5 of a formulation in gel form

Using the preparation process previously described for the adhesive compositions in gel form, 5 different examples of adhesive composition according to the present invention were prepared in gel form indicated in Table 1 below.

Table 1

<table>
<thead>
<tr>
<th>WATER</th>
<th>Ex. 1</th>
<th>Ex. 2</th>
<th>Ex. 3</th>
<th>Ex. 4</th>
<th>Ex. 5</th>
</tr>
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<td>XANTHAN GUM</td>
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<td>54.80</td>
<td>54.70</td>
<td>53.70</td>
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<td>0.20</td>
<td>0.30</td>
<td>0.30</td>
<td>0.20</td>
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<td>38.00</td>
<td>40.00</td>
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<td>MONOPROPYLENE GLYCOL</td>
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<td>3.00</td>
<td>3.00</td>
<td>3.00</td>
<td>3.00</td>
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<tr>
<td>COCONUT DIETHANOLAMIDE</td>
<td>2.00</td>
<td>2.00</td>
<td>2.00</td>
<td>2.00</td>
<td>2.00</td>
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<td>LAURIC MONOETHANOLAMIDE</td>
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<td>8.88</td>
<td>8.88</td>
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<tr>
<td>PERFUME</td>
<td>5.00</td>
<td>5.00</td>
<td>5.00</td>
<td>5.00</td>
<td>5.00</td>
</tr>
<tr>
<td>TOTAL</td>
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<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
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<tr>
<td>VISCOSITY (Pa·s)</td>
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<td>3340</td>
<td>3100</td>
<td>1600</td>
<td>2250</td>
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In the case, for example, of an adhesive composition in gel form according to the present invention to be used as adhesive deodorant/detergent for WCs, a fundamental characteristic is the duration of the same in the WC subjected to water flushings: a formulation such as that indicated in Table 1 as Example 2, applied to a WC with a dimension of about 10 grams, has an average duration of 100 flushings, i.e. about 7 days, considering an average of 15 water flushings a day in an average family composed of 4 persons.

By adding lauric monoethanolamide or PEG distearate to this composition (see Example 1 or 4), it is possible to increase the duration with time up to 15 days or even 1 month. By adding coconut diethanolamide (see Table 1, Example 3), on the other hand, the duration of the tablet can be shortened even up to one day only in addition to giving the formulation a cleaning and/or foaming action.

In use in dishwashers and washing machines, it is also important for the adhesive composition according to the present invention not to produce too much foam and monopropylene glycol can therefore be inserted (see Table 1, Example 5) as solvent in the composition. In this example, in fact, the cleaning action of the coconut diethanolamide is maintained, reducing however its foaminess thanks to the presence of the solvent.
Examples 6-11 of a formulation in solid form

[0086] Using the preparation process previously described for the adhesive compositions in solid form, six different examples of adhesive composition according to the present invention were prepared in solid form indicated in Table 2 below.

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<th>Ex.8</th>
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<th>Ex.10</th>
<th>Ex.11</th>
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<td>60.00</td>
<td>40.00</td>
<td>40.00</td>
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<tr>
<td>ZETASAP</td>
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<td></td>
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<td></td>
<td>5.00</td>
<td></td>
</tr>
<tr>
<td>PERFUME</td>
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<td>4.00</td>
<td>5.00</td>
<td>4.00</td>
<td>5.00</td>
<td>5.00</td>
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<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

[0087] As is evident from the above table, the adhesive composition according to the present invention in solid form is obtained (see Table 2, Examples 8 to 11) using a particular mixture of surfactants such as soaps, lauryl ether sulfates and solvents, commercialized with the name Zetasap C11 by Zschimmer & Schwartz, commercialized by Zschimmer & Schwartz, which in this case is a mixture of propylene glycol, soap, anionic surfactant (sodium Laureth Sulfate), sorbitol, glycerine and sequestrants.

[0088] Also in the case of adhesive compositions in solid form, depending on the destination of final use, other components can be added with the purpose of modulating the duration of the adhesive composition with time, modifying the cleaning and/or foaming properties and melting point of the product.

[0089] In use in dishwashers or washing machines, a certain quantity of solvent must be added to abate the foam produced by the detergent element Zetasap (see Table 2, Example 10), whereas in order to increase the hardness of the adhesive composition in solid form (tablet) and consequently its duration in WCs, PEG is added (see Table 2, Example 9). In order to reduce the hardness and therefore the duration of the adhesive composition in solid form (tablet), on the contrary, coconut diethanolamide can be added (see Table 2, Example 11).

[0090] In use as a perfumer for the environment, on the other hand, the duration of the adhesive composition in solid form (tablet) must be much greater and, as the adhesive composition is not subjected to water flushings, an extremely hard formulation is selected (see Table 2, Example 6).

Example 12 (comparative)

[0091] The adhesive compositions based on ethoxylated amine in gel form according to the present invention have a greater adhesiveness with respect to the compositions known in the state of the art.

[0092] The adhesiveness of the compositions of Example 2 and 4 was measured experimentally and compared with that of an adhesive cleaning composition in gel form available on the market and containing, as adhesion promoter, a non-ionic surfactant (ethoxylated alcohol).

[0093] The adhesiveness was measured with a TAXTplus structure analyzer produced by StableMicroSystems.

[0094] A first measurement of the adhesiveness (Test 1) of the compositions was effected as follows. The cylindrical probe having a diameter of 10 mm of the analyzer was lowered onto the sample at a rate of 1 mm/s, penetrating the sample for a distance of 10 mm. The probe is then brought to the starting position at a rate of 1 mm/s. With this test, the hardness of the sample (max force) is evaluated, during the descending phase, together with the penetration level (consistency); during the reascending of the probe, the minimum force (in negative value) and the adhesiveness (negative area).

[0095] The results of Test 1 are indicated in Table 3. The values indicated in the table correspond to the average value of three measurements.
From Test 1, it is clear that the composition according to the present invention (adhesion promoter: ethoxylated amine) is much more resistant to penetration and detains the probe longer during the reascending phase (greater adhesion) with respect to the composition according to the known art (adhesion promoter: non-ionic surfactant).

A second measurement of the adhesiveness of the compositions (Test 2) was effected as follows. A sample of the composition is deposited on the base of the instrument. The sample is compressed to 90% of its dimensions with a cylindrical probe made of Plexiglas (diameter 25 mm); a force of 2 kg is maintained on the sample, by means of the probe, for 10 seconds, the probe then reascends to its starting position. With this test, the adhesiveness of the sample to the probe is measured.

The results of Test 2 are indicated in Table 4. The values indicated in the table correspond to the average value of three measurements.

### Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Max force [g]</th>
<th>Consistency [g·sec]</th>
<th>Min force [g]</th>
<th>Adhesiveness [g·sec]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 2</td>
<td>650.585</td>
<td>4137.195</td>
<td>-569.163</td>
<td>-4019.546</td>
</tr>
<tr>
<td>Example 2 standard deviation</td>
<td>37.936</td>
<td>379.728</td>
<td>24.834</td>
<td>321.375</td>
</tr>
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<td>419.316</td>
<td>2641.533</td>
<td>-370.716</td>
<td>-2758.157</td>
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<tr>
<td>Reference standard deviation</td>
<td>36.952</td>
<td>237.391</td>
<td>29.709</td>
<td>134.668</td>
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</tbody>
</table>

### Table 4

<table>
<thead>
<tr>
<th>Sample</th>
<th>Max force [g]</th>
<th>Adhesiveness [g·sec]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 2</td>
<td>3569.443</td>
<td>561.87</td>
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<tr>
<td>Example 2 standard deviation</td>
<td>70.774</td>
<td>98.069</td>
</tr>
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<td>Example 4</td>
<td>4303.815</td>
<td>350.142</td>
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<tr>
<td>Example 4 standard deviation</td>
<td>83.719</td>
<td>56.444</td>
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<tr>
<td>Reference</td>
<td>3276.106</td>
<td>274.227</td>
</tr>
<tr>
<td>Reference standard deviation</td>
<td>30.179</td>
<td>12.138</td>
</tr>
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</table>

Test 2 shows that the product with the greatest adhesiveness is the sample of Example 2 based on ethoxylated amine. A further composition based on ethoxylated amine, Example 4, has higher maximum force values (detaching force), as it adheres better to the Plexiglas probe. In any case, the reference sample, based on non-ionic surfactant, is the least adhesive and least resistant among the samples tested.

### Claims

1. An adhesive composition cleaning and/or perfuming and/or hygienizing in solid, gel, or paste form, characterized in that comprises:
   i) an adhesion promoter selected from at least one amine having formula (I)
wherein

- R and R₁, the same or different, represent a linear or branched, saturated or unsaturated alkyl chain, with a number of carbon atoms varying from C₁₂ to C₂₂, preferably from C₈ to C₁₈, alternatively, one of the substituents

R or R₁ represent a -(CₘH₂ₘO)ₙH group;

- m varies from 2 to 4,
- with an alkoxylation equal to x or x+y, varying from 15 to 50 alkoxyl moles, preferably from 20 to 40, even more preferably from 25 to 35;

ii) a perfuming agent,
iii) possibly a cleaning/foaming agent.

2. The adhesive composition according to claim 1, characterized by having a viscosity ranging from 1,500 Pa·s to 5,000 Pa·s, preferably from 2,000 Pa·s to 4,000 Pa·s.

3. The adhesive composition according to any of the previous claims, characterized in that the alkoxy is selected from ethylene oxide, propylene oxide, butylene oxide with mixed alkoxylation in random and/or block combinations.

4. The adhesive composition according to any of the previous claims, characterized in that the amine having formula (I) is an ethoxylated amine or an ethoxylated-propoxylated amine.

5. The adhesive composition according to any of the previous claims, characterized in that it comprises an alkanolamide selected from the compounds having formula (II)

\[
\text{RN} \\
\text{R₁} \\
\text{(I)}
\]

wherein

- R and R₁, the same or different, represent a linear or branched, saturated or unsaturated alkyl chain, with a number of carbon atoms varying from C₁₂ to C₂₂, preferably from C₈ to C₁₈, alternatively, one of the substituents

R or R₁ represent a -(CₘH₂ₘO)ₙH group;

- m varies from 2 to 4,
- with an alkoxylation equal to x or x+y, varying from 15 to 50 alkoxyl moles, preferably from 20 to 40, even more preferably from 25 to 35;

ii) a perfuming agent,
iii) possibly a cleaning/foaming agent.

6. The adhesive composition according to claim 5, characterized in that the alkanolamide having formula (II) is a lauric monoethanolamide or coconut diethanolamide.

7. The adhesive composition according to any of the previous claims, characterized in that component (iii) is selected from alkanolamides having formula (II), anionic- and/or non-ionic- and/or amphoteric-based surfactant
mixtures, and/or solvent mixtures based on propylene glycol, glycerine and mixtures of sequestrants such as phosphonates, Edta, citrates, phosphates, preferably alkano- amides having formula (II).

8. The adhesive composition according to any of the previous claims, characterized in that it comprise one or more thickening agents selected from xanthan gums, hydroxethyl cellulose, acrylic polymers or copolymers, polyethylene glycol or polyethylene glycol distearates having a molecular weight ranging from 200 to 8,000, solvents such as propylene glycol, glycerol triacetate, C_5-C_20 alcohols, preferably C_{10}-C_{15}.

9. The adhesive composition according to any of the previous claims, in the form of a gel, comprising the alkoxylated amine having formula (I) in a quantity ranging from 20 to 60% by weight with respect to the total weight of the composition, a thickening agent in a quantity ranging from 0 to 5% by weight with respect to the total weight of the composition, a perfuming agent in a quantity ranging from 1 to 10% by weight with respect to the total weight of the composition and water in a quantity ranging from 79 to 25% by weight with respect to the total weight of the composition.

10. The adhesive composition according to any of the previous claims from 1 to 8, in the form of a solid or paste, comprising the alkoxylated amine having formula (I) in a quantity ranging from 20 to 76% by weight with respect to the total weight of the composition, an alkano amide having formula (II) or another cleaning and/or solidifying agent as component iii) in a quantity ranging from 10 to 70% by weight with respect to the total weight of the composition, a perfuming agent in a quantity ranging from 1 to 10% by weight with respect to the total weight of the composition.

11. A process for the preparation of an adhesive cleaning and/or perfuming and/or hygienizing composition, in the form of a solid, gel or paste, comprising i) an adhesion promoter selected from at least one amine having formula (I)

\[
\begin{align*}
R \quad \text{RN} \\
\text{R}_1 \\
\text{(I)}
\end{align*}
\]

wherein \( R \) and \( \text{R}_1 \), the same or different, represent a linear or branched, saturated or unsaturated alkyl chain, with a number of carbon atoms varying from C_{12} to C_{22}, preferably from C_6 to C_{18}, alternatively, one of the substituents \( R \) or \( \text{R}_1 \) represents a \( -(\text{C}_m\text{H}_2\text{mO})_y\text{H} \) group;

- \( m \) varies from 2 to 4,

with an alkoxylation equal to \( x \) or \( x+y \), varying from 15 to 50 moles of alkoxy, preferably from 20 to 40, even more preferably from 25 to 35, and

ii) a perfuming agent,

iii) possibly a cleaning/foaming agent,

said process comprising the following operative phases:

- heating a solidifying component, when present, for obtaining the adhesive composition in solid form, to a temperature higher than its melting point;
- incorporating component i), component iii), when present, and any further component of the composition into the melt, in any order, or directly dissolving in water, when the first phase of the process is absent, on the condition that the perfuming agent ii) is added last,
- homogenizing the composition by mixing at a temperature ranging from 35°C to 55°C for a time varying from 5 to 30 minutes,
- pouring the composition into a container,
- cooling the composition until solidification or the formation of a gel.

12. Use of an adhesive composition in the form of a solid, gel or paste, according to any of the claims from 1 to 10,
for cleaning, and/or disinfecting and/or perfuming by application onto the surface of interest, of sanitary fixtures, household appliances, walls, furniture.

13. A process for applying an adhesive composition according to any of the claims from 1 to 10, characterized in that said composition is applied directly to the surface of interest, to which it adheres without the need for supports and/or containers.
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<tr>
<th>Category</th>
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<td>X</td>
<td>GB 2 194 957 A (BRISTOL MYERS CO BRISTOL MYERS CO [US]; SQUIBB BRISTOL MYERS CO [US]) 23 March 1988 (1988-03-23) * page 1, paragraph 1; claim 1; table VIII *</td>
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<td>EP 0 268 967 A2 (HENKEL KGAA [DE]) 1 June 1988 (1988-06-01) * page 2, line 36 - line 39; claims 1-10 *</td>
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The present search report has been drawn up for all claims

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<td>The Hague</td>
<td>25 January 2011</td>
<td>Richards, Michael</td>
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- **X**: particularly relevant if taken alone
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- **A**: technological background
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- **P**: intermediate document
- **T**: theory or principle underlying the invention
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- **L**: document cited for other reasons
- **S**: member of the same patent family, corresponding document
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25-01-2011

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<td>11-04-1989</td>
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For more details about this annex: see Official Journal of the European Patent Office, No. 12/82
REFERENCES CITED IN THE DESCRIPTION

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