(57) Abrégé/Abstract:
The invention relates to the use of water-insoluble organopolysiloxane derivatives of the general formula (I) (see formula I) in which the radicals \( R^1 \) are alkyl radicals having 1 to 4 carbon atoms or aryl radicals, but at least 80% of the radicals \( R^1 \) are methyl radicals, and \( R^2 \) at least once in the molecule has the definition (a) (see formula II) for defoaming aqueous media, especially printing inks and paints.
Abstract:

The invention relates to the use of water-insoluble organopolysiloxane derivatives of the general formula (I)

\[
\begin{align*}
R^1 & \quad \text{Si-O} \quad R^1 \\
R^2 & \quad \text{Si-O} \quad R^2 \\
R^1 & \quad \text{Si-O} \quad R^1
\end{align*}
\]

in which the radicals

- \( R^1 \) are alkyl radicals having 1 to 4 carbon atoms or aryl radicals, but at least 80% of the radicals \( R^1 \) are methyl radicals, and
- \( R^2 \) at least once in the molecule has the definition (a)

\[
\begin{align*}
\text{R}^3 \quad \text{O} \quad \text{O} \quad \text{O} \\
\text{R}^3 \quad \text{O} \quad \text{O} \quad \text{O}
\end{align*}
\]

for defoaming aqueous media, especially printing inks and paints.
Organopolysiloxanes for defoaming aqueous systems

The invention relates to the use of organopolysiloxane copolymers as defoamers for aqueous coating systems and printing inks.

Increasing numbers of coating materials and printing inks are being reformulated on an aqueous basis for greater environmental acceptability.

Because of the ingredients used – emulsifiers, wetting agents, and dispersing additives – such formulations have a strong tendency to stabilize foam. This is manifested to adverse effect not only during the production of these paints and inks but also more particularly during their application, when large quantities of air are introduced and the esthetics and physical properties of the final coatings are impaired. Consequently, in virtually all water-based systems the use of antifoams or defoamers is widespread and often indispensable.

In the past a large number of formulations have been described which envisage the use of, for example, silicone oils, organically modified siloxanes, hydrophobic polyoxyalkylene, mineral oils, natural oils, and other hydrophobic liquids as defoaming substances. Frequently combinations of the abovementioned substances with hydrophobic solids, such as silicas, metal stearates or fatty acid amides, for example, are also used, which often reinforce the foam-inhibiting or defoaming effect.

The use of silicone oils, especially dimethylpolysiloxanes of low to medium viscosity, for the defoaming of aqueous solutions
or dispersions is known and is described in, for example, the book by W. Noll "Chemie und Technologie der Silicone".

It is likewise known to use polyoxyalkylene-polysiloxane copolymers as defoamers. US-A-3 763 021 describes a typical preparation for defoaming of aqueous latices, consisting of

(1) from 1 to 20% by weight of a siloxane glycol copolymer of the general formula

\[
\begin{align*}
&\text{CH}_3 \quad \text{Si} \quad \text{Si} \quad \text{O} \quad \text{Si} \quad \text{O} \quad \text{Si} \quad \text{CH}_3 \\
&\text{CH}_3 \quad \text{CH}_3 \quad \text{x} \quad \text{G} \quad \text{y} \quad \text{CH}_3
\end{align*}
\]

in which

\begin{align*}
x & \text{ has an average value of from 6 to 420 and} \\
y & \text{ has an average value of from 3 to 30, and} \\
G & \text{ is a radical of the structure} \\
& -D(\text{OR})_2A, \\
D & \text{ is an alkyene radical,} \\
R & \text{ is composed of ethylene radicals and propylene or butylene radicals in a ratio of ethylene radicals to the other alkyene radicals such that the ratio of carbon atoms to oxygen atoms in all blocks OR is in the range from 2.3 : 1 to 2.8 : 1,} \\
z & \text{ has an average value of from 25 to 100, and} \\
A & \text{ is a capping group,}
\end{align*}
(2) from 65 to 98% by weight of polypropylene glycol having an average molecular weight in the range from 1,000 to 2,000, and
(3) from 1 to 15% by weight of a hydrophobic silica.


According to the present state of knowledge the defoaming activity depends critically on the ability of a defoamer to penetrate the foam lamellae and thereby to destabilize them until they burst (K. Koczo, J.K. Koczone, D.T. Wasan, J. Colloid Interface Sci. 166, 225 to 238 (1994)). For this to be achieved there must be a controlled incompatibility (hydrophobicity) with the aqueous phase in which defoaming is to take place. This is because a defoamer, if it is too compatible (hydrophilic), will no longer be able to be very effective, since it will not preferentially penetrate the foam lamella. If the incompatibility is too great, the defoaming is generally very good but is frequently accompanied in that case by unwanted side effects including surface defects, adverse effects on wetting behavior, and separation phenomena.

Accordingly, the search for a suitable defoamer always involves a search for the right balance between compatibility and incompatibility for the system in which defoaming is to take place, with the objective of coming as close as possible to the target hydrophobicity/hydrophilicity equilibrium. The ongoing concern to reduce VOC (volatile organic component) levels, coupled with the desire to prevent the fogging problems on interior walls that are caused by low-volatility mineral oils or conventional plasticizers, by more effective formulating, have led to a situation where a large number of traditional
product designs for the defoaming of aqueous coating systems nowadays appear unsuitable.

DE-A-40 32 006 teaches a method of defoaming and/or degassing organic systems by adding an antifoam comprising an organopolysiloxane to the organic system, which may consist of diesel oil or crude oil or products from the cracking of the oil. The organopolysiloxane used is a polymer composed of siloxane units of the general formulae

\[ R_1 SiO_{(4-a)/2} \quad \text{and} \quad R_3 A_2 SiO_{4-(b+c)/2} \]

in which

- \( R \) is a monovalent hydrocarbon radical having 1 to 18 carbon atoms per radical,
- \( A \) is a radical of the general formula

\[
\begin{array}{c}
\text{CH}_3 \chi (R^1 O (R^2) H)_x \\
\text{CH}_2 \chi (R^1 O (R^2) H)_y
\end{array}
\]

in which

- \( R^1 \) is a radical of the formula
  \(-\text{CR}^3 \text{H},\)
- \( R^3 \) is hydrogen or a monovalent organic radical,
- \( R \) is a radical of the formula
  \(-\text{CR}^4 \text{H}-\text{CH}_3 \text{ or } -\text{(CH}_2)_3,\)
- \( R^4 \) is hydrogen or a monovalent organic radical,

- \( v, w \) are each 0 or an integer, \( v + w \) being on average from 0 to 16,
- \( x, y \) are 0 or 1, \( x + y \) being 1 or 2,

\( a \) is 1, 2 or 3,
\( b \) is 0, 1 or 2, and
\( c \) is 1 or 2, the sum \( b + c \) being not greater than 3.

The siloxanyl-alkenediy1-bis-ω-hydroxypolyoxyalkylenes used themselves and their preparation are described in patent DD-A-2 55 737.

Adducts of alkynediol derivatives with hydrogen-functional siloxanes are therefore known.

From DE-A-195 16 30 and DE-A-43 43 235, moreover, derivatives are known which in addition to the alkynediol (alkoxylates) also describe other radicals, examples being polyether radicals, for the derivatization of the hydrogen siloxanes. These copolymers are also employed for defoaming apolar phases, such as diesel fuels.

It is an object of the present invention, however, to provide organopolysiloxanes which are particularly suitable for defoaming aqueous media and which allow the above-described desirable incompatibility/compatibility balance to be set in a targeted way while allowing significantly improved balances and ensuring much more rapid foam collapse.

This object is surprisingly achieved through the use of water-insoluble organopolysiloxane derivatives of the general formula (I) for defoaming aqueous media:

\[
\begin{align*}
\text{R}^1 & \quad \left[ \begin{array}{c}
\text{R}^1 \\
\text{R}^2 \\
\text{Si-O} \\
\text{R}^1 \\
\end{array} \right] \\
\text{R}^2 & \quad \left[ \begin{array}{c}
\text{Si-O} \\
\text{R}^2 \\
\text{Si-R}^2 \\
\end{array} \right] \\
\text{Si-R}^1 & \quad \left[ \begin{array}{c}
\text{Si-O} \\
\text{R}^1 \\
\text{Si-R}^1 \\
\end{array} \right] \\
\end{align*}
\]
where the radicals
R\(^1\) are alkyl radicals having 1 to 4 carbon atoms or aryl radicals, but at least 80\% of the radicals R\(^1\) are methyl radicals,

R\(^2\) in the molecule are identical or different and can have the following definitions:

(a)

\[
\begin{align*}
\text{R}^2 & \text{C}^0 \text{(CH}_2\text{CH}_2\text{O)}_d \text{H}_2\text{C}^\text{-CH-O-}_e \text{R}^4 \\
\text{R}^3 & \text{C}^0 \text{(H}_2\text{C}^\text{-CH}_2\text{O)}_d \text{H}_2\text{C}^\text{-CH-O-}_e \text{R}^4
\end{align*}
\]

in which
R\(^3\) is a hydrogen or alkyl radical,
R\(^4\) is a hydrogen, alkyl or carboxyl radical,
c is a number from 1 to 20,
d is a number from 0 to 50,
e is a number from 0 to 50

or

(b)

\[-(\text{CH}_2^-)_4\text{OR}^5,\]
in which

R^5 is a hydrogen, alkyl or carboxyl radical or a dimethylol propane radical containing ether groups if desired, and

f is a number from 2 to 20

or

c)

- (CH\textsubscript{-})\textsubscript{g} (OC\textsubscript{2}H\textsubscript{4}H\textsubscript{-})\textsubscript{h} (OC\textsubscript{3}H\textsubscript{6}H\textsubscript{-})\textsubscript{j} (OC\textsubscript{4}H\textsubscript{8}H\textsubscript{-})\textsubscript{i} (OCH\textsubscript{2} CH(C\textsubscript{6}H\textsubscript{5})\textsubscript{v})\textsubscript{k} OR^6

in which

R^6 is a hydrogen, alkyl or carboxyl radical,
g is a number from 2 to 6,
h is a number from 0 to 20,
i is a number from 1 to 50,
j is a number from 0 to 10,
k is a number from 0 to 10

or

(d)

correspond to the radical R^1,
with the proviso that in the average molecule at least one radical R^2 has the definition (a),

a is a number from 1 to 500, preferably from 1 to 200, and in particular from 1 to 50, and
b is a number from 0 to 10, preferably < 5, and in particular 0.

The siloxane framework can be straight-chain (b = 0) or else branched (> 0 to 10). The value of b and also the value of a are to be understood as average values in the polymer molecule, since the polysiloxanes for use in accordance with the invention are in the form of - generally - equilibrated
mixtures. The skilled worker is well aware that, owing to their polymeric nature, the compounds are in the form of a mixture having a distribution which is governed essentially by the laws of statistics. The values for all indices therefore represent average values.

The radicals $R^3$ are alkyl radicals having 1 to 4 carbon atoms, such as methyl, ethyl, propyl or butyl radicals, or aryl radicals, in which case the phenyl radicals are preferred. For reasons of preparation and price the methyl radicals are preferred, and so at least 80% of the radicals $R^3$ are methyl radicals. Particular preference is given to those polysiloxanes in which all of the radicals $R^1$ are methyl radicals.

$R^2$ in the molecule can be identical or different with the proviso that in the average molecule at least one radical $R^2$ has the definition (a). The radicals $R^2$ are detailed below.

In the radical (a)

\[
\begin{align*}
R^3 & = \text{a hydrogen or alkyl radical, in particular a lower alkyl radical having 1 to 4 carbon atoms. Preference is given to hydrogen.} \\
R^4 & = \text{a hydrogen, alkyl or carboxyl radical, in particular an acyl radical. In one particular embodiment $R^4$ is a hydrogen. The index} \\
c & = \text{a number from 1 to 20, preferably 1. The indices} \\
d \text{ and } e & = \text{are independently of one another integers from 0 to 50. Preference is given to a radical (a) in which $R^3$ and $R^4$ are}
\end{align*}
\]
hydrogens, the index c is 1, and the indices d and e independently of one another are each from 0 to 10. These indices are, as the skilled worker is aware, average numbers, since it is known that the addition reaction of alkylene oxides such as ethylene oxide and propylene oxide onto alcohols produces a mixture of compounds with different chain lengths. These radicals (a) may be introduced into the molecule of the polysiloxane by addition reaction of correspondingly substituted alkyne derivative precursors onto SiH groups of a prior art polysiloxane in the presence of a hydrosilylation catalyst.

In the radical (b)

\[-\text{(CH}_2\text{)}_f\text{OR}_5\]

\(R^5\) is a hydrogen, alkyl or carboxyl radical or a dimethylolpropane radical with or without ether groups. Preferably \(R^5\) is a hydrogen radical or a dimethylolpropane derivative. The index \(f\) is a simple number from 2 to 20, the numerical values from 3 to 6 being preferred. These radicals (b) may be introduced by means of a hydrosilylation reaction as already described above, by addition of alkenols or their derivatives onto SiH groups of the organopolysiloxane. Examples of such alkenols are allyl alcohol, hexenol or, for example, trimethylolpropane monoallyl ether.

In the radical (c)

\[-\text{(CH}_2\text{)}_g(\text{OC}_2\text{H}_4\text{)}_h(\text{OC}_3\text{H}_6\text{)}_i(\text{OC}_4\text{H}_8\text{)}_j\text{OC}_2\text{H} \text{(C}_6\text{H}_5\text{)}_k\text{OR}_6\]

\(R^6\) is a hydrogen, alkyl or carboxyl radical. Preferably \(R^6\) is a hydrogen or methyl radical. The index \(g\) is a number from 2 to 6, the index \(h\) is a number from 0 to 20, the index
i is a number from 1 to 50, the index
j is a number from 0 to 10, and the index
k is a number from 0 to 10.

Preferably the index g has a value of 3, the index h a value from 0 to 12, and the index i a value from 8 to 30, and the indices j and k are preferably < 5, in particular 0.

The radicals (c) as well may be introduced by means of a hydrosilylation reaction as already described above, by addition reaction of alkenyl polyethers or their derivatives onto SiH groups of the organopolysiloxane.

Alternatively (d) the radical R² may also correspond to the radical R¹, in which case, again, the methyl radical is particularly preferred.

The compounds of the general formula (I) are industrial products whose incompatibility with the aqueous phase in which defoaming is to take place (hydrophobicity) is custom-tailored by way of the nature (structure) of the individual components and/or their fragments and their relative proportions in the molecule as a whole in such a way that the reaction products are insoluble in water - that is, form clear solutions in water to an extent of not more than 20 g/l, preferably < 10 g/l, and in particular less than about 5 g/l.

The key relationships affecting structure/hydrophilicity/hydrophobicity are known to the skilled worker in the field of interface chemistry, as are the corresponding synthesis methods. Optimization measures can therefore be taken on the basis of a few rangefinding experiments.

In the examples below the preparation of organofunctionally modified organopolysiloxanes for use in accordance with the invention, of the formula I, is shown first of all.
The products prepared in these examples are designated E1 to E7.

Example E1

In a 250 ml four-necked flask equipped with KPG stirrer, dropping funnel, intensive condenser and nitrogen blanketing 51.15 g of Golpanol® BEO (butynediol etherified with about 1.1 mol of ethylene oxide) together with 11.0 g of a pendant hydrogen siloxane (SiH content: 4.62 eq/kg) are heated to 140°C with stirring and a catalyst consisting of H₂PtCl₆·6H₂O and RuCl₃·H₂O in isopropanol (corresponding to 10 ppm of Pt and 10 ppm of Ru based on the overall batch) is added. Within a few minutes the SiC linking reaction begins, the exothermic nature of which reaction is intensified by successive dropwise addition of the major amount of SiH-siloxane (44 g) for about 50 to 60 minutes. After around just 20 minutes the result of volumetric gas analysis on a sample is evidence of quantitative SiH conversion.

A clear, amber-colored liquid having a viscosity of 639 mPas at 25°C is isolated.

Example E2

Following the procedure of Example 1, 42.52 g of Golpanol BEO together with 12.0 g of a pendant hydrogen siloxane (SiH content: 3.52 eq/kg) are heated to 140°C with stirring and a catalyst consisting of H₂PtCl₆·6H₂O and RuCl₃·H₂O in isopropanol (corresponding to 10 ppm of Pt and 10 ppm of Ru based on the overall batch) is added. The remaining amount of SiH siloxane (48 g) is added dropwise within 60 minutes. At the end of dropwise addition the SiH conversion determined from volumetric gas analysis is quantitative.
The reaction mixture is cooled to give a clear, amber-colored liquid having a viscosity of 896 mPas at 25°C.

Example E3

In accordance with the procedure employed in Example 1 42.39 g of Golpanol BEO together with 12 g of a pendant hydrogen siloxane (SiH content: 3.51 eq/kg; chain length: 20, degree of functionalization: 5) are heated to 140°C with stirring and a catalyst solution consisting of H₂PtCl₆·6H₂O and RuCl₃H₂O in isopropanol (corresponding to 10 ppm of Pt and 10 ppm of Ru based on the overall batch) is added. Following the addition of the major amount of hydrogen siloxane (48 g) the mixture is clear and shows no SiH hydrogen detectable by volumetric gas analysis. The viscosity of the honey-colored Golpanol BEO siloxane copolymer is 1.717 mPas at 25°C.

Example E4

To prepare an ABA-structured, Golpanol BEO siloxane block copolymer, working in analogy to Example E1, 39.51 g of Golpanol BEO together with 13.0 g of an α,ω-dihydopolydimethylsiloxane (SiH content: 3.02 eq/kg, chain length: 9.1) are charged to a vessel with stirring at 140°C and a catalyst solution consisting of H₂PtCl₆·6H₂O and RuCl₃H₂O in isopropanol (corresponding to 10 ppm of Pt and 10 ppm of Ru based on the overall batch) is added. Over the course of an hour the major amount of the linear hydrogen siloxane (52 g) is added dropwise, with SiH conversion already being found quantitative at the end of the metered addition. Cooling gives a clear, amber-colored liquid having a viscosity of 207 mPas at 25°C.
Example E5

In a 250 ml four-necked flask equipped with KPG stirrer, dropping funnel, intensive condenser and nitrogen blanketing 42.31 g of Golpanol BEO together with 50.0 g of a pendant hydrogen siloxane (SiH content: 4.67 eq/kg) and 8.62 g of an allyl polyether (M : 382 g/mol) are heated to 120°C with stirring and 25 ppm of Karstedt catalyst are added. Over the course of 85 minutes following addition of the catalyst the reaction mixture attains quantitative SiH conversion. The liquid isolated is clear and amber-yellow.

Example E6

An inertized apparatus analogous to that of Example E5 is charged with 36.28 g of Golpanol BMP (monopropoxylated diol) together with 13 g of a pendant hydrogen siloxane (SiH content: 3.52 eq/kg) at 135°C with stirring and a catalyst solution consisting of H₂PtCl₆·6H₂O and RuCl₃·H₂O in isopropanol (corresponding to 10 ppm of Pt and 10 ppm of Ru based on the overall batch) is added. Over the course of an hour the remaining 52 g of the hydrogen siloxane are added dropwise. After 70 minutes the clear reaction mixture attains quantitative SiH conversion. A yellow copolymer is obtained.

Example E7

A 250 ml four-necked flask equipped with KPG stirrer, dropping funnel, intensive condenser and nitrogen blanketing is charged with 50.0 g of a pendant hydrogen siloxane (SiH content: 4.67 eq/kg) at 140°C with stirring and a catalyst solution consisting of H₂PtCl₆·6H₂O and RuCl₃·H₂O in isopropanol (corresponding to 10 ppm of Pt and 10 ppm of Ru based on the
overall batch) is added. Over the course of 20 minutes 40.34 g of trimethylolpropane monoallyl ether diacetate and then over the course of 15 minutes, 15.65 g of Golpanol BEO are added dropwise. After the end of dropwise addition the batch is held at reaction temperature with stirring for 1 hour. Determination of SiH by volumetric gas analysis shows an SiH conversion of 99.2%.

The clear yellow product is a liquid having a viscosity of 279 mPas.

Examples of organopolysiloxanes for use in accordance with the invention are products having the following average structures:

where

\[ R^2 \] corresponds for example in each case to the radical

\[
\text{CH}_3\left(\text{H}_2\text{C}\cdot\text{CH}_2\text{O}\right)_1\left(\text{H}_2\text{C} \cdot \text{CH}_2\text{O}\right)_0\cdot\text{H}
\]

\[
\text{CH}_3\left(\text{H}_2\text{C}\cdot\text{CH}_2\text{O}\right)_1\left(\text{H}_2\text{C} \cdot \text{CH}_2\text{O}\right)_0\cdot\text{H}
\]
The organopolysiloxanes for use in accordance with the invention can be employed, for example, for the defoaming of polymer dispersions, paints, and printing inks.

For their inventive use as defoamers of aqueous media these organopolysiloxanes can be added directly in concentrations of from 0.01 to 3.0% by weight to the aqueous systems in which defoaming is to take place. An alternative option is to formulate these derivatives beforehand by for example dispersing organic or inorganic solids such as silicas, alumina, alkaline earth metal carbonates, alkaline earth metal salts of long-chain fatty acids, their amides or urea derivatives in these prior art siloxanes. The defoamers for use in accordance with the invention can also be employed in the form of their aqueous emulsions. Emulsions are frequently employed with preference on account of their greater ease of metering and the fact that droplet distributions are already established. Particular preference is given in this context to defoamer emulsions whose average particle diameter lies between 1 and 10 µm. Such emulsions may then contain between 5 and 50% by weight of the components for use in accordance with the invention.

These organopolysiloxanes for use in accordance with the invention may of course also be formulated together with other, prior art defoamer oils, such as silicone oils, polyether siloxanes, fatty alcohol derivatives or fatty acid derivatives or polyethers, for example.

The invention is illustrated below by means of examples. Examined for this purpose are the organopolysiloxanes E1 to E7 for use in accordance with the invention and also the comparison defoamers V8 Tego® Foamex 810 (Degussa), V9 Dehydran® 1293 (solution of a polyether siloxane copolymer; Cognis), and V10 Surfynol® 104 (Tetramethyldecylnediol; Air Products).
The performance properties of the various compounds of the invention or compounds for use in accordance with the invention are examined using the following test systems, in which the amounts are in percent by weight:
Aqueous test systems:

1.) Solid-color aqueous base coat

<table>
<thead>
<tr>
<th>Compound</th>
<th>Amount</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Daotan VTW 6462 (TM)</td>
<td>26.0</td>
<td>dispersion of a urethane acrylate hybrid</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Solutia)</td>
</tr>
<tr>
<td>Water</td>
<td>10.0</td>
<td></td>
</tr>
<tr>
<td>AMP 90</td>
<td>0.2</td>
<td>aminomethylpropanol (Angus)</td>
</tr>
<tr>
<td>Viskalex HV 3 (TM)</td>
<td>1.6</td>
<td>acrylate thickener</td>
</tr>
<tr>
<td>Water</td>
<td>30.0</td>
<td></td>
</tr>
<tr>
<td>Black dye</td>
<td>4.4</td>
<td></td>
</tr>
<tr>
<td>Viacryl VSC 6254 (TM)</td>
<td>5.8</td>
<td>styrene acrylic dispersion</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Solutia)</td>
</tr>
<tr>
<td>Water</td>
<td>21.8</td>
<td></td>
</tr>
</tbody>
</table>

0.2% by weight in each case of the inventive and noninventive defoamers, as the final formula ingredient, are incorporated by dispersion at 1000 rpm using a perforated disk for 2 minutes. 45 g of the paint are then poured into a graduated cylinder and measurements are made of the foam height in ml and of the time taken for the foam to collapse to a residual volume of < 1 ml. The remaining, prior art paint material is then applied on a cathodic electrocoat primer, and following a flash-off time of 10 minutes at room temperature the system is baked first at 80°C for 10 minutes and finally at 140°C for 20 minutes. The dry coating is inspected for surface defects. Assessment is made on a scale from 1 to 6, where 1 describes a defect-free film while 6 attests to severe wetting defects.

2.) Surfacer formula

<table>
<thead>
<tr>
<th>Compound</th>
<th>Amount</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resydrol VAZ (TM)</td>
<td>23.0</td>
<td>alkyd resin (Solutia)</td>
</tr>
<tr>
<td>5541W/42WA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dispers 750 W</td>
<td>1.5</td>
<td>dispersing additive (Tego)</td>
</tr>
<tr>
<td>Butylglycol</td>
<td>1.5</td>
<td></td>
</tr>
</tbody>
</table>
N-methylpyrrolidone 1.0
Kronos 2190 14.0 titanium dioxide (Kronos)
Blanc fixe micro 14.0 filler (Omya)
5
Printex U 0.2 carbon black (Degussa)
Resydrol VAZ
5541W/42WA 42.5 alkyd resin (Solutia)
Water 2.0

0.3% by weight of each of the inventive and noninventive defoamers, as the final formula ingredient, is incorporated by dispersion at 3000 rpm using a toothed-wheel disk for 3 minutes. 45 g of the paint are then poured into a graduated cylinder and measurements are made of the foam height in ml and of the time taken for the foam to collapse to a residual volume of < 1 ml. Thereafter the remaining, prior art paint material is applied to a cathodic electrocoat primer, and after a flash-off time of 10 minutes at room temperature the system is baked first at 80°C for 10 minutes and finally at 160°C for 25 minutes. The dry coating is assessed visually as described above.

3) Overprint varnish:

<p>| | | |</p>
<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>Joncryl™ 8085</td>
<td>39.8</td>
<td>styrene acrylic solution (Johnson Polymer)</td>
</tr>
<tr>
<td>Joncryl 90</td>
<td>35.9</td>
<td>styrene acrylic dispersion (Johnson Polymer)</td>
</tr>
<tr>
<td>Joncryl 77</td>
<td>9.7</td>
<td>acrylate emulsion (Johnson Polymer)</td>
</tr>
<tr>
<td>Jonwax™ 35</td>
<td>4.9</td>
<td>polyethylene wax emulsion (Johnson Polymer)</td>
</tr>
<tr>
<td>Butylglycol</td>
<td>4.9</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>3.9</td>
<td></td>
</tr>
</tbody>
</table>
The print varnish is formulated in accordance with the formula above. The final formula ingredient added is in each case 0.2% by weight of the inventive and noninventive defoamers, incorporation taking place at 1500 rpm using a bead mill disk for 3 minutes. Subsequently, once again, 45 g are weighed out into a standing cylinder and the foam height in ml is recorded. The time taken for the foam height to fall below 1 ml is measured. Thereafter the remainder of the print varnish is knifecoated onto a transparent PVC sheet using a 12 µ spiral applicator. Any wetting defects induced by the defoamer are evaluated as described above on a scale from 1 to 6.

Test system 1:
(Solid-color aqueous basecoat)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Foam height in ml/45 g</th>
<th>Foam breakdown time in s.</th>
<th>Wetting (scale 1-6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>77</td>
<td>&gt; 1 000</td>
<td>2</td>
</tr>
<tr>
<td>E1</td>
<td>48</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>E2</td>
<td>45</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>E3</td>
<td>47</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>E4</td>
<td>47</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>E5</td>
<td>48</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>E6</td>
<td>45</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>E7</td>
<td>45</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Surfynol 104</td>
<td>54</td>
<td>20</td>
<td>2</td>
</tr>
<tr>
<td>Foamex 810</td>
<td>45</td>
<td>15</td>
<td>5</td>
</tr>
<tr>
<td>Dehydram 1293</td>
<td>57</td>
<td>150</td>
<td>4</td>
</tr>
</tbody>
</table>
Test system 2:
(Surfacer)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Foam height in ml/45 g</th>
<th>Foam breakdown time in s.</th>
<th>Wetting (scale 1-6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>78</td>
<td>&gt; 500</td>
<td>2</td>
</tr>
<tr>
<td>E1</td>
<td>50</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>E2</td>
<td>49</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>E3</td>
<td>47</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>E4</td>
<td>51</td>
<td>15</td>
<td>1</td>
</tr>
<tr>
<td>E5</td>
<td>53</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>E6</td>
<td>49</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>E7</td>
<td>47</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>Surfynol 104</td>
<td>53</td>
<td>60</td>
<td>3</td>
</tr>
<tr>
<td>Foamex 810</td>
<td>49</td>
<td>100</td>
<td>5</td>
</tr>
<tr>
<td>Dehydran 1293</td>
<td>54</td>
<td>220</td>
<td>3</td>
</tr>
</tbody>
</table>
Test system 3:
(aqueous overprint varnish)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Foam height in ml/45 g</th>
<th>Foam breakdown time in s.</th>
<th>Wetting (scale 1-6)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>82</td>
<td>&gt; 2 000</td>
<td>2</td>
</tr>
<tr>
<td>E1</td>
<td>48</td>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td>E2</td>
<td>51</td>
<td>15</td>
<td>2</td>
</tr>
<tr>
<td>E3</td>
<td>46</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>E4</td>
<td>49</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>E5</td>
<td>50</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>E6</td>
<td>49</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>E7</td>
<td>47</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>Surfynol 104</td>
<td>47</td>
<td>50</td>
<td>2</td>
</tr>
<tr>
<td>Foamex 810</td>
<td>45</td>
<td>50</td>
<td>5</td>
</tr>
<tr>
<td>Dehydran 1293</td>
<td>54</td>
<td>100</td>
<td>3</td>
</tr>
</tbody>
</table>

As can be seen from the test results described above the siloxane derivatives for use in accordance with the invention feature effective foam suppression coupled with extremely rapid foam destruction without the appearance of the wetting defects that other defoamers induce. They accordingly achieve an innovative balance between compatibility and incompatibility unachievable to date with prior art defoamers.
The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method for defoaming aqueous media which comprises adding to the aqueous media an organopolysiloxane derivative of the general average formula (I):

   \[
   \begin{array}{c}
   \text{R}^1 \quad \text{Si-O} \quad \text{Si-O} \quad \text{Si-R}^2 \\
   \text{R}^1 \quad \text{Si-O} \quad \text{Si-O} \quad \text{Si-R}^2 \\
   \text{R}^1 \quad \text{Si-O} \quad \text{Si-O} \quad \text{Si-R}^2 \\
   \text{R}^1 \quad \text{Si-O} \quad \text{Si-O} \quad \text{Si-R}^2 \\
   \end{array}
   \]

wherein:

- \text{R}^1 at each occurrence is a C\textsubscript{1}-C\textsubscript{4} alkyl radical or an aryl radical, wherein at least 80% of the \text{R}^1 radicals are methyl radicals;

- \text{R}^2 radicals in the molecule are identical or different and at each occurrence \text{R}^2 has the following definition:

   \[
   \begin{array}{c}
   \text{R}^3 \quad \text{CH}_3 \\
   \text{CH}_c \quad \text{O-} \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{O-d} \quad \text{CH}_3 \quad \text{CH}_c \quad \text{O-e} \quad \text{R}^4 \\
   \text{R}^3 \quad \text{CH}_c \quad \text{O-} \quad \text{CH}_3 \quad \text{CH}_2 \quad \text{O-d} \quad \text{CH}_3 \quad \text{CH}_c \quad \text{O-e} \quad \text{R}^4 \\
   \end{array}
   \]

wherein:

- \text{R}^1 is hydrogen or an alkyl radical;
- \text{R}^4 is hydrogen, an alkyl radical or a carboxyl radical;
- \text{c} is a number from 1 to 20;
- \text{d} is a number from 0 to 50; and
- \text{e} is a number from 0 to 50;
(b) 
\[-(\text{CH}_2^-)_f \text{OR}^5\]
wherein:
\[\text{R}^5\] is hydrogen, an alkyl radical or a carboxyl radical or a dimethylol propane radical containing ether groups if desired; and
\[f\] is a number from 2 to 20;
(c) 
\[-(\text{CH}_2^-)_g (\text{OC}_2\text{H}_4^-)_h (\text{OC}_3\text{H}_6^-)_i (\text{OC}_4\text{H}_8)_j (\text{OCH}_2\text{CH(C}_6\text{H}_5))_k \text{OR}^6\]
wherein:
\[\text{R}^6\] is hydrogen, an alkyl radical or a carboxyl radical;
\[g\] is a number from 2 to 6;
\[h\] is a number from 0 to 20;
\[i\] is a number from 1 to 50;
\[j\] is a number from 0 to 10;
\[k\] is a number from 0 to 10; or
(d) \[\text{R}^1\], with the proviso that in the average molecule at least one radical \[\text{R}^2\] has the definition (a);
wherein:
\[a\] is a number from 1 to 500; and
\[b\] is a number from 0 to 10; and
wherein the water solubility of the organopolysiloxane is such that it forms a clear solution in water in an amount not more than 20 g/l at 25° C.

2. The method according to claim 1, where \(b=0\) in the organopolysiloxane derivative.

3. The method according to claim 1, wherein in the organopolysiloxane derivative the radicals \(\text{R}^3\) are methyl radicals, \(a=1\) to 50 and \(b=0\).
4. The method according to claim 1, 2 or 3, wherein $R^3$ is hydrogen in the organopolysiloxane derivative.

5. The method according to any one of claims 1 to 4, wherein $R^4$ is hydrogen or an acyl radical in the organopolysiloxane derivative.

6. The method according to any one of claims 1 to 5, wherein the index $c=1$ or 2, and $d$ and $e$ independently of one another are from 0 to 10 in the organopolysiloxane derivative.

7. The method according to any one of claims 1 to 6, wherein $R^6$ is hydrogen or a methyl radical, $g=3$, $h=0$ to 12, $i=8$ to 30 and $j$ and $k$ independently of one another are $<5$, in the organopolysiloxane derivative.

8. The method according to claim 7, where $j$ and $k$ are zero in the organopolysiloxane derivative.

9. The method according to any one of claims 1 to 8, wherein the organopolysiloxane forms a clear solution in water in an amount not more than 5 g/l.

10. The method according to any one of claims 1 to 9, wherein the aqueous media is an aqueous surfactant system.

11. The method according to any one of claims 1 to 9, wherein the aqueous media is a printing ink or an ink.

12. The method according to any one of claims 1 to 9, wherein the aqueous media is an aqueous coating material.
13. The method according to any one of claims 1 to 9, wherein the aqueous media is a polymer dispersion.

14. The method according to claim 1, wherein the organopolysiloxane has an average structure which is:

```
CH₃
R²-Si-O-Si-O-Si-R²;
CH₃
```

```
H₃C-Si-O-Si-O-Si-R²;
CH₃
```

```
CH₃
R²-Si-O-Si-O-Si-O-Si-CH₃;
CH₃
```

```
CH₃
CH₃
R²-Si-O-Si-O-Si-R²;
```

or

```
CH₃
R²-Si-O-Si-O-Si-O-Si-R²;
```

wherein:

R² is a radical of the formula

```
CH₂-O-(H₃C-CH₂-O)ₙ-(H₃C-CH₂-O)ₙ-H
```

```
CH₂-O-(H₂C-CH₂-O)ₙ-(H₂C-CH₂-O)ₙ-H.
```

15. A method for defoaming aqueous media which comprises adding to the aqueous media an organopolysiloxane derivative of the general average formula (I):
wherein:

$R^1$ is at each occurrence an alkyl radical having 1 to 4 carbon atoms or an aryl radical, wherein at least 80% of the $R^1$ radicals are methyl radicals;

$R^2$ radicals in the molecule are identical or different and at each occurrence $R^2$ has the following definition:

$\begin{align*}
&\left(\text{CH}_2\right)_c\text{O}\left(\text{CH}=-\text{CH}_2\text{O}\right)_d\text{H}_2\text{C}=-\text{CH}=-\text{O}\right)_e\text{R}^4 \\
&\left(\text{CH}_2\right)_c\text{O}\left(\text{H}_2\text{C}=-\text{CH}_2\text{O}\right)_d\text{H}_2\text{C}=-\text{CH}=-\text{O}\right)_e\text{R}^4
\end{align*}$

wherein:

$R^3$ is hydrogen or an alkyl radical;

$R^4$ is hydrogen, an alkyl radical or a carbonyl radical;

$c$ is a number from 1 to 20;

$d$ is a number from 0 to 50;

$e$ is a number from 0 to 50;

(b)

$-(\text{CH}_2\text{-})_e\text{OR}^5$

wherein:

$R^5$ is hydrogen, an alkyl radical or a carboxyl radical, or a dimethylol propane radical containing ether groups if desired; and
f is a number from 2 to 20;

(c) \[-(CH_2-)_g(OC_2H_4-)_h(OC_3H_6-)_i(OC_4H_8)_j\]

\((OCH_2CH(C_6H_5))_kOR^6\)

wherein:
- \(R^6\) is hydrogen, an alkyl radical or a carboxyl radical;
- \(g\) is a number from 2 to 6;
- \(h\) is a number from 0 to 20;
- \(i\) is a number from 1 to 50;
- \(j\) is a number from 0 to 10;
- \(k\) is a number from 0 to 10; or

(d) \(R^1\), with the proviso that in the average molecule at least one radical \(R^2\) has the definition (a);

wherein:
- \(a\) is a number from 1 to 500; and
- \(b\) is a number from 0 to 10; and

wherein the water solubility of the organopolysiloxane is such that forms a clear solution in water in an amount not more than 20 g/l at 25°C.

16. A defoamer emulsion, which comprises:

from about 5 to about 50% of at least one water-insoluble organopolysiloxane derivative of the general average formula (I):

\[
\begin{array}{c}
R^2 \quad Si \quad O \quad \left[ \begin{array}{c}
R^1 \\
Si \quad O \\
R^1
\end{array} \right] \quad \left[ \begin{array}{c}
R^1 \\
Si \quad O \\
R^1
\end{array} \right] \quad \left[ \begin{array}{c}
R^1 \\
Si \quad R^2 \\
R^1
\end{array} \right] \\
\quad \left[ \begin{array}{c}
R^1-truncated \\
Si \quad O \\
R^1
\end{array} \right] \quad \left[ \begin{array}{c}
R^1-truncated \\
Si \quad O \\
R^1
\end{array} \right] \quad \left[ \begin{array}{c}
R^1-truncated \\
Si \quad R^2 \\
R^1
\end{array} \right]
\end{array}
\]

\(1\)
wherein:

$R^1$ at each occurrence is a $C_1$-$C_4$ alkyl radical or an aryl radical, wherein at least 80% of the $R^1$ radicals are methyl radicals;

$R^2$ radicals in the molecule are identical or different and at each occurrence $R^2$ has the following definition:

\[
\begin{align*}
&\text{(a)} \quad \text{c} \quad \text{d} \quad \text{e} \\
&\begin{array}{c}
\text{CH}_3 \\
\text{R}^3 \\
\text{CH}_3 \\
\text{R}^3 \\
\text{R}^3
\end{array}
\end{align*}
\]

\[
\begin{align*}
&\text{(a)} \quad \text{c} \quad \text{d} \quad \text{e} \\
&\begin{array}{c}
\text{CH}_3 \\
\text{R}^3 \\
\text{CH}_3 \\
\text{R}^3 \\
\text{R}^3
\end{array}
\end{align*}
\]

wherein:

$R^3$ is hydrogen, or an alkyl radical;

$R^1$ is hydrogen, an alkyl radical or a carbonyl radical;

c is a number from 1 to 20;

d is a number from 0 to 50;

e is a number from 0 to 50;

\[
\text{(b)} \quad -(\text{CH}_2-)_{f}\text{OR}^5
\]

wherein:

$R^5$ is hydrogen, an alkyl radical or a carboxyl radical, or a dimethylol propane radical containing ether groups if desired; and

$f$ is a number from 2 to 20;

\[
\text{(c)} \quad -(\text{CH}_2-)_{g}(\text{OC}_2\text{H}_4-)_{h}(\text{OC}_3\text{H}_6-)_{j}(\text{OCH}_2\text{CH}(\text{C}_6\text{H}_5))_{k}\text{OR}^6
\]

wherein:

$R^6$ is hydrogen, an alkyl radical or a carboxyl radical;

g is a number from 2 to 6;

$h$ is a number from 0 to 20;

$i$ is a number from 1 to 50;

$j$ is a number from 0 to 10;
k is a number from 0 to 10; or
(d) \( R^1 \), with the proviso that in the average molecule at least one radical \( R^2 \) has the definition (a);
  a is a number from 1 to 500; and
  b is a number from 0 to 10; and
  wherein the organopolysiloxane forms a clear solution in water in an amount not more that 20 g/l at 25° C.;
  water; and
  optionally an auxiliary or additive.

17. An ink or a paint which comprise a pigment and a defoam emulsion as defined in claim 16.

18. A polymer dispersion which comprises a polymer and a defoam emulsion as defined in claim 16.

19. An aqueous coating material which comprises an emulsion as defined in claim 16.