Mold-release agent composition for aluminum die-casting.

Mold-release agent composition for aluminum die casting comprising an aqueous emulsion wherein the emulsified phase comprises a liquid polyorganosiloxane, an extreme-pressure lubricant and an emulsifying agent exhibit an excellent mold-release performance and excellent extreme-pressure lubrication capacity (oil-film strength).
The present invention relates to an emulsion-type mold-release agent composition for use in aluminum die-casting. More particularly, this invention relates to an emulsion type mold release agent having excellent storage stability, mechanical stability and which exhibits both a release function and an extreme-pressure lubricating function.

Alkyl-modified organopolysiloxanes, aralkyl-modified organopolysiloxanes, carboxyl-modified organopolysiloxanes, and carboxylate ester-modified organopolysiloxanes are widely used as mold-release agents in the automotive industry.

However, these organopolysiloxanes, while generally having excellent mold-release properties, exhibit poor extreme-pressure lubricating properties and also perform inadequately as mold-release agents when applied to the intricate dies or molds used in aluminum die-casting. As a consequence, the development is desired of a mold-release agent for application in aluminum die-casting that has an even better mold-release performance and that also exhibits an excellent extreme-pressure lubricating performance.

During molding by aluminum die-casting, molten aluminum is injected under high pressure into the cavity of an intricate mold or die, and as a consequence the oil film will have a reduced strength (fissures are produced in the oil film) when the mold-release agent used for this service has a low extreme-pressure lubricating capacity. As a result, the aluminum molding will have a diminished releasability and the aluminum itself will have a diminished hot runnability or transferability. It is for these reasons that a mold-release agent is required that has an excellent extreme-pressure lubricating capacity as well as an improved mold-release capacity.

United States Patent No. 3,759,827, which issued to Groenhof et al. on Sept 18, 1973 describes lubricant compositions consisting essentially of an alkyl ester of chlorendic acid and a liquid polydiorganosiloxane wherein the organic groups bonded to the silicon atoms are hydrocarbon or halogenated hydrocarbon radicals. The silicon-bonded hydrocarbon radicals preferably contain fewer than 18 carbon atoms, and all of these hydrocarbon radicals are most preferably methyl.

The problem solved by the present invention is achieved by using as a mold release agent an aqueous emulsion comprising a known extreme pressure lubricant selected from organic compounds containing sulfur, halogen or phosphorus and a polydiorganosiloxane wherein one of the organic groups bonded to a portion of the repeating units and/or the terminal units are hydrocarbon radicals containing at least 8 carbon atoms or ester groups.

This invention provides a mold release composition for use in aluminum die casting, said composition comprising an aqueous emulsion wherein the non-aqueous phase comprises

(A) 100 weight parts of a liquid polyorganosiloxane of the general formula

wherein each R is individually selected from the group consisting of phenyl radicals and or monovalent aliphatic hydrocarbon radicals containing no more than 7 carbon atoms, with the proviso at least 50 mole percent of the radicals represented by R are methyl, R1 represent an alkyl or aralkyl radical containing at least 8 carbon atoms, -R2COOH, -R3COOR+, or -R5OOCRG group, wherein R2, R3, and R5 are divalent hydrocarbon radicals, R+ and RG are monovalent hydrocarbon radicals, A is R or R1 with the proviso that A is R when x is zero, x is an integer with a value of zero to 50, y is an integer with a value of 10 to 450, the sum of x and y is from 10 to 500, and the integer represented by x is smaller than the integer represented by y; and

(B) from 0.5 to 50 weight parts of an extreme-pressure lubricant selected from sulfur-containing organic compounds, halogen-containing organic compounds, and phosphorus-containing organic compounds, where said emulsion contains an emulsifying agent in an amount sufficient to stabilize said emulsified phase.

To explain the present compositions in greater detail, the liquid polyorganosiloxane comprising ingredient A is the main or principal ingredient of the non-aqueous phase of the present compositions. Each of
the R groups in the preceding formula for this ingredient represents a monovalent hydrocarbon radical containing no more than 7 carbon atoms. These radicals are exemplified by alkyl radicals such as methyl, ethyl, propyl, and butyl, and by the phenyl group, cyclohexyl group, and vinyl group. Methyl preferably constitutes at least 50 mole\% of the R radicals, most preferably 100\%.

R in the preceding formula is an alkyl group or aralkyl radical containing at least 8 carbon atoms or the \(-R_2\text{COOH}, -R_3\text{COOR}^4\), or \(-R_5\text{OOCR}^6\) group in order to increase the paintability, mold-release capacity, and compatibility with the other organic starting ingredients. \(R^2, R^3, \text{ and } R^6\) in these formulae represent monovalent hydrocarbon radicals and \(R^4\) represent monovalent hydrocarbon radicals.

From the standpoint of the paintability and compatibility with other organic substances, \(R^2, \text{ and } R^6\) are preferably alkylene radicals and the total number of carbon atoms in \(R^2\), the combination of \(R^3\) and \(R^4\), and the combination of \(R^5\) and \(R^6\) is at least 10.

The substituent represented by A is R or R\(^1\), but is restricted to R when x is zero.

The unit

\[
\begin{array}{c}
R \\
\text{SiO}^- \\
R^1
\end{array}
\]

in the preceding formula is exemplified by but not limited to units with the formulae

\[
\begin{array}{c}
\text{CH}_3 \\
\text{SiO}^- \\
R^7
\end{array}
\]

where \(R^7\) is an alkyl or aralkyl radical containing at least 8 carbon atoms,

\[
\begin{array}{c}
\text{CH}_3 \\
\text{SiO}^- \\
R^2 \text{COOH}
\end{array}
\]

units with the formula

\[
\begin{array}{c}
\text{CH}_3 \\
\text{SiO}^- \\
R^3 \text{COOR}^4
\end{array}
\]

and units with the formula

\[
\begin{array}{c}
\text{CH}_3 \\
\text{SiO}^- \\
R^5 \text{OOCR}^6
\end{array}
\]
The molecules of ingredient A can contain two or three of these units. Excessively large values of x are associated with a poor paintability, paint crawling or cissing, and so forth, and for this reason the value of x should fall within the range of 0 to 50.

The value of y should be at least 10 based on paintability considerations, but should not exceed 450 based on considerations of emulsifiability. The sum of x and y should not exceed 500 because the viscosity is too high and emulsification becomes problematic. Finally, the value of x should be less than the value of y based on paintability considerations. In preferred species of ingredient A, R^1 includes the -R^2COOH, -R^2COOR^4, or -R^2OOCR^6 group wherein R^2, R^3, and R^4 represent alkyl radicals, R^4 and R^6 represent alkyl radicals, and the number of carbon atoms in R^2, the combination of R^3 and R^4, and the combination of R^5 and R^6, is in each case at least 10. This preferred polyorganosiloxane undergoes orientation on the mold surface and thereby provides an even greater improvement in mold-release capacity.

Ingredient A is readily synthesized by the following method: using a catalyst such as chloroplatinic acid, etc., for example, a liquid methylhydrogenpolysiloxane or a dimethylsiloxane-methylhydrogensiloxane copolymer is addition-reacted with, for example, an alpha-olefin such as CH\_2 = CH(CH\_2)\_10CH\_3, styrene or alpha-methylstyrene, an unsaturated aliphatic acid such as CH\_2 = CH(\text{CH}_\_2)\_8COOH, or an unsaturated aliphatic acid ester such as CH\_2 = CH(\text{CH}_\_2)\_8COOC\_3H\_7 or CH\_2 = CHCH\_2OOC\_11H\_23.

The extreme-pressure lubricant referred to as ingredient B of the present compositions not only operates to provide an extreme-pressure lubrication capacity (oil-film strength), but also improves the mold-release capacity of the present compositions.

Ingredient B is an extreme-pressure lubricant selected from sulfur-containing organic compounds, halogen-containing organic compounds, and phosphorus-containing organic compounds. The sulfur-containing organic compounds are exemplified by but not limited to sulfurized oils and pastes such as sulfurized dipentene with the structure

\[
\begin{align*}
\text{CH}_3 \text{ (CH}_2\text{)} \_5 \text{CH - CH (CH}_2\text{)} \_x \text{ CO - OR'}
\end{align*}
\]

sulfurized sperm oils of the formula

\[
\text{C}_6\text{H}_5 - \text{CH}_2 - \text{S - S - CH}_2 - \text{C}_6\text{H}_5
\]

were R' represents an alkyl radical; by sulfides such as dibenzyl disulfide

\[
\text{(CH}_3\text{)}\_3\text{C - S - S - C(CH}_3\text{)}\_3;
\]

and di-tert-butyl disulfide

and by thiocarbonates with, for example, the following structure
The halogen-containing organic compounds are exemplified by but not limited to chlorinated hydrocarbons such as chlorinated paraffins, chlorinated naphthalenes, chlorinated carboxylic acid derivatives such as methyl trichlorostearate (Cl₃C(CH₂)₁₄COOCH₃), dioctyl chlorendate (Cl₂C(C₈H₁₇)₂COOC₈H₁₇), dibutyl chlorendate; iodine compounds such as benzyl iodide; and by perfluoroalkyl-containing hydrocarbon compounds.

The phosphorus-containing organic compound suitable for use as ingredient B include but are not limited to organic compounds exemplified by phosphates and phosphites such as tricresyl phosphate (C₆H₅PO₃) and dilauryl phosphite (C₁₂H₂₅O)₂PHO.

When the extreme-pressure lubricant is a liquid or paste, it can be dissolved or dispersed to homogeneity in ingredient A using a stirrer. When the extreme-pressure lubricant is a solid at room temperature, it can be dispersed to homogeneity by first mixing it with ingredient A and then stirring with heating above the melting point of the mixture.

The extreme-pressure lubricating capacity (oil-film strength) will be inadequate when too little extreme-pressure lubricant comprising component (B) is present. The presence of too much extreme-pressure lubricant results in the following disadvantages: (a) the emulsion suffers from a loss of storage stability, dilution stability, and mechanical stability; (b) the relative concentration of ingredient A is reduced and the mold-release capability then becomes inadequate; and (c) the heat resistance is also diminished. For these reasons the concentration of ingredient B should be from 0.5 to 50 parts by weight, preferably from 1 to 20 parts by weight, per 100 parts by weight of ingredient A.

The extreme-pressure lubricants may, of course, be used in combinations of two or more types.

The aluminum die-casting composition (ADC) or mold-release agent composition of the present invention is prepared by emulsifying ingredients A and B in water using an emulsifying agent. Suitable emulsifying agents for this purpose include but are not limited to non-ionic surfactants, anionic surfactants, and cationic surfactants. The non-ionic surfactants are exemplified by polyoxyalkylene alkyl ethers,
polyoxyalkylene alkylphenol ethers, polyoxyalkylene alkyl esters, sorbitan alkyl esters, polyoxyalkylene sorbitan alkyl esters, polyethylene glycols, and polypropylene glycols.

The cationic surfactants are exemplified by quaternary ammonium hydroxides such as octyltrimethylammonium hydroxide, dodecytrimethylammonium hydroxide, hexadecyltrimethylammonium hydroxide, octyldimethylbenzylammonium hydroxide, decyldimethylbenzylammonium hydroxide, dioctadecyldimethylammonium hydroxide, beef tallow trimethylammonium hydroxide, and cocotrimethylammonium hydroxide, and by salts of these hydroxides.

The anionic surfactants are exemplified by sodium, potassium, lithium, and amino salts of higher fatty acids such as stearic acid, oleic acid, lauric acid; alkylbenzenesulfonic acids such as hexylbenzenesulfonic acid, octylbenzenesulfonic acid, decylbenzenesulfonic acid, cetylbenzenesulfonic acid, and myristylbenzenesulfonic acid; the sulfate esters of polyoxyethylene monoalkyl ethers such as

\[
\text{CH}_3\text{(CH}_2\text{)}_n\text{CH}_2\text{O(C}_2\text{H}_4\text{O)}_m\text{SO}_3\text{H},
\]

\[
\text{CH}_3\text{(CH}_2\text{)}_n\text{O(C}_2\text{H}_4\text{O)}_m\text{SO}_3\text{H},
\]

\[
\text{CH}_3\text{(CH}_2\text{)}_n\text{CH}_2\text{O(C}_2\text{H}_4\text{O)}_m\text{SO}_3\text{H},
\]

\[
\text{CH}_2\text{(CH}_2\text{)}_n\text{CH}_2\text{C}_6\text{H}_4\text{O(C}_2\text{H}_4\text{O)}_m\text{SO}_3\text{H};
\]

and the alkynaphthylsulfonic acids.

Among the metal salts of higher fatty acids, the alkali metal salts function as potentiating emulsifying agents that augment the extreme-pressure lubricant.

This emulsifying agent is generally a non-ionic surfactant alone or in combination with an anionic surfactant or a cationic surfactant.

While the ADC mold-release composition of the present invention can include only the water-based emulsion of ingredients A and B, it may also contain preservatives, mold inhibitors, and rust inhibitors. These additives are exemplified by but not limited to sodium benzoate, potassium benzoate, sodium sorbate, potassium sorbate, sodium dehydroacetate, potassium dehydroacetate and sodium nitrite.

The ADC mold-release composition of the present invention may also contain one or more of the following ingredients, with the proviso that they do not interfere with the objectives of the present invention: colorants, mineral oils, higher fatty acids, thickeners, aluminum powder, and graphite.

The ADC mold-release emulsion composition according to the present invention is readily prepared by first blending, for example, from 30 to 55 weight percent of ingredient A with 2 to 10 weight percent of ingredient B, 5 to 9 weight percent of emulsifying agent, 0.3 to 0.5 weight percent each of a preservative, a mold inhibitor, and a rust inhibitor, and 62.7 to 27.5 weight percent water and by then emulsifying this blend using a suitable emulsification device such as a homogenizer, colloid mill, line mixer, homomixer, or sonolator.

The present ADC mold-release emulsion compositions are generally used by uniformly spraying them onto the surface of the aluminum die-casting mold or die using a spray machine.

The present invention is explained in greater detail through the following illustrative examples, which should not be interpreted as limiting the scope of the invention as defined in the accompanying claims. In the examples all parts and percentages are by weight and viscosities are measured at 25 °C.

The structures and viscosities of the polyorganosiloxanes used in the examples are as follows:

(A)
The extreme-pressure lubricants used in the examples are:
(a) tricresyl phosphate

(b) dioctyl chlorendate
The following methods were used to measure the properties of the polyorganosiloxane emulsion compositions prepared in the examples and comparison examples.

**Paintability**

The polyorganosiloxane emulsion composition was diluted 50-fold with water and then uniformly sprayed on clay-coated paper using a simple spray gun. After drying at room temperature, uniformly spaced lines were drawn with an oil-based, broad-tipped marker using a ruler. Blurring of the lines was evaluated according to the following scale.

- + + absolutely no blurring of the lines, uniform adhesion of the ink
- + minor blurring of parts of the lines, moderately nonuniform adhesion of the ink
- x substantial line blurring

**Mold-Releaseability**

The polyorganosiloxane emulsion composition was diluted 5-fold with water and then sprayed into a mold with internal dimensions of 5 cm x 5 cm, depth = 5 mm). The bottom of the mold contained multiple grooves in a castellated configuration. The mold was preheated to approximately 350 °C, and molten aluminum that had been melted at a temperature of approximately 750 °C in an electric furnace was injected into the mold. After cooling, the aluminum molding was stripped from the mold, and the mold-releaseability was evaluated based on the ease of separation of the casting from the mold.

- + + + superior separation from the mold
- + + good separation from the mold
- + fair separation from the mold
- x difficult separation from the mold
Storage Stability of the Emulsion

180 cc of the polyorganosiloxane emulsion composition were introduced into a 200 cc-capacity glass jar, and the stability was evaluated after standing for 3 months at room temperature (25 °C).

Dilution Stability of the Emulsion

The polyorganosiloxane emulsion composition was diluted with tap water to a polyorganosiloxane concentration of 1%, equivalent to a 50-fold dilution based on the initial polyorganosiloxane concentration of 50%. After the diluted emulsion was stored for 2 days at room temperature in a 200 cc glass jar, it was inspected for oil floating to the surface, creaming, and other defects.

Mechanical Stability of the Emulsion

The polyorganosiloxane emulsion composition was diluted with tap water to a polyorganosiloxane concentration of 1%, and 500 cc of the dilution was introduced into a 1 L beaker. The dilution was then treated with a homogenizer for 30 minutes at 5,000 rpm. After coming to quiescence, the dilution was inspected for oil sticking to the beaker walls and oil floating on the surface at the top of the beaker.

Evaluation of Extreme-Pressure Lubrication Capacity

The organopolysiloxane emulsion composition was measured under the following conditions in accordance with the Method for Testing the Load Resistance of Lubricating Oils described in JIS K-2519, and the seizure load (kg) was calculated. The specifications for the test stand were:

- Apparatus: 4-ball wear tester from Shinkoh Zohki Kabushiki Kaisha
- Steel Balls: 3/4" steel balls for ball-bearing service, diameter = 19.05 mm, high-grade based on JIS B-1501
- Load By Test Steel Ball: 1,000 kg maximum
- Spindle RPM: 750rpm
- Direction of Spindle Rotation: Clockwise when viewed top-to-bottom

Example 1

Into each of 5 beakers were added 50 parts polyorganosiloxane A and 4 parts of one of the five extreme-pressure lubricants (a) through (e), respectively, with stirring to homogeneity. This was followed by addition of the emulsifying agent with stirring to homogeneity using a stirrer. The emulsifying agent consisted of 4 parts polyethylene glycol monolauryl ether containing an average of 6 oxyethylene units per molecule and 1.0 part of the sodium salt of the sulfate ester of a polyethylene glycol monolauryl ether containing an average of 4.5 oxyethylene units per molecule. To this mixture was subsequently added 5 parts water followed by stirring and emulsification by passage through a colloid mill emulsification apparatus. 36 parts water were then added to the resultant emulsion with dissolution to homogeneity, thereby yielding the final polyorganosiloxane emulsion composition.

The properties of this composition were measured, and the results are reported in Table 1.

Comparison Example 1

An organopolysiloxane emulsion composition was prepared as described in Example 1, but in the present case omitting the addition of the extreme-pressure lubricant. The properties of this composition were measured as in the same manner as the emulsion of Example 1, and these results are also reported in Table 1. The results in Table 1 demonstrate that the compositions of the present invention provided substantially improved (by approximately 1.6-fold) extreme-pressure lubrication capacities (seizure load) and exhibited superior mold-releasability.
Example 2

Polyorganosiloxane emulsion compositions were prepared as described in Example 1, but in this example using organopolysiloxanes B, C, and D in place of the polyorganosiloxane A in Example 1 and adding 4 parts extreme-pressure lubricant (a) in each preparation. For the purposes of comparison, the same organopolysiloxane emulsion compositions were prepared without the addition of the extreme-pressure lubricant. The properties of these compositions were measured as in Example 1, and these results are reported in Table 2.
Example 3

An organopolysiloxane emulsion composition was again prepared as in Example 1, but in this example the extreme-pressure lubricants (a) through (e) used in Example 1 were replaced with the combination of

<table>
<thead>
<tr>
<th>Organopolysiloxane</th>
<th>Extreme Pressure Lubricant</th>
<th>Paintability</th>
<th>Wear Resistability</th>
<th>Storage Stability</th>
<th>Dilution Stability</th>
<th>Mechanical Stability</th>
<th>Stress Load (kg)</th>
<th>Global Evaluation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present Invention</td>
<td>a</td>
<td>++</td>
<td>+++</td>
<td>excellent</td>
<td>excellent</td>
<td>excellent</td>
<td>150</td>
<td>superior</td>
</tr>
<tr>
<td>C</td>
<td>a</td>
<td>++</td>
<td>+++</td>
<td>excellent</td>
<td>excellent</td>
<td>excellent</td>
<td>140</td>
<td>superior</td>
</tr>
<tr>
<td>B</td>
<td>None</td>
<td>None</td>
<td>excellent</td>
<td>excellent</td>
<td>excellent</td>
<td>excellent</td>
<td>90</td>
<td>unsatisfactory</td>
</tr>
<tr>
<td>D</td>
<td>None</td>
<td>None</td>
<td>excellent</td>
<td>excellent</td>
<td>excellent</td>
<td>excellent</td>
<td>80</td>
<td>unsatisfactory</td>
</tr>
<tr>
<td>E</td>
<td>None</td>
<td>None</td>
<td>excellent</td>
<td>excellent</td>
<td>excellent</td>
<td>excellent</td>
<td>80</td>
<td>unsatisfactory</td>
</tr>
</tbody>
</table>
3.5 parts extreme-pressure lubricant (a) and 1.5 parts extreme-pressure lubricant (e). For the purposes of comparison, the same organopolysiloxane emulsion composition was prepared without the addition of the extreme-pressure lubricant. The properties of these compositions were measured, and these results are reported in Table 3.

The data in Table 3 demonstrate that the composition of the present invention has a very strong extreme-pressure lubricating performance and also an excellent mold-release performance and is therefore highly qualified for application as a mold-release agent for aluminum die-casting.

Table 3

<table>
<thead>
<tr>
<th></th>
<th>Present Invention</th>
<th>Comparison Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organopolysiloxane</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>Extreme Pressure Lubricant</td>
<td>a and e combination</td>
<td>None</td>
</tr>
<tr>
<td>Paintability</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>Mold Releasability</td>
<td>++</td>
<td>+</td>
</tr>
<tr>
<td>Storage Stability</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Dilution Stability</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>Seizure Load (kg)</td>
<td>150</td>
<td>80</td>
</tr>
<tr>
<td>Global Evaluation</td>
<td>Superior</td>
<td>Unsatisfactory</td>
</tr>
</tbody>
</table>

Example 4

Organopolysiloxane emulsion compositions were prepared in the same manner as the composition of Example 1, but in this example replacing the 4 parts extreme-pressure lubricant (a) in Example 1 with 0.1 part, 1 part, 5 parts, 10 parts, 25 parts, and 50 parts extreme-pressure lubricant (a) per 100 parts of polyorganosiloxane A.

For purposes of comparison, an organopolysiloxane emulsion composition was prepared as above without the addition of the extreme-pressure lubricant. The properties of these compositions were measured, and the results are reported in Table 4. These results demonstrate that the compositions of the present invention were excellent, well-balanced ADC mold-release agents. However, the extreme-pressure lubricating capacity was inadequate at 0.1 parts extreme-pressure lubricant. Moreover, the addition of more than 50 parts extreme-pressure lubricant resulted in a poor emulsion storage stability and was therefore unsuitable for ADC mold-release agents.
1. A mold-release agent composition for use in aluminum die-casting, said composition comprising an aqueous emulsion wherein the non-aqueous phase comprises

<table>
<thead>
<tr>
<th></th>
<th>Present Invention</th>
<th>Comparison Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 Part</td>
<td>5 Parts</td>
</tr>
<tr>
<td>Storage Stability</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>Seizure Load (mp)</td>
<td>120</td>
<td>130</td>
</tr>
<tr>
<td>Mold Releasability</td>
<td>++</td>
<td>+++</td>
</tr>
<tr>
<td>Global Evaluation</td>
<td>Superior</td>
<td>Superior</td>
</tr>
</tbody>
</table>
(A) 100 weight parts of a polyorganosiloxane of the formula

\[
\begin{array}{c}
\text{A} - \text{SiO}_{(\text{SiO})_x (\text{SiO})_y}\text{Si} - \text{A} \\
\text{R} \text{ R} \text{ R} \text{ R} \text{ R} \\
\text{R} \text{ R} \text{ R} \text{ R} \text{ R}
\end{array}
\]

wherein each R is individually selected from the group consisting of phenyl radicals and monovalent aliphatic hydrocarbon radicals group containing no more than 7 carbon atoms, with the proviso that methyl comprises at least 50 mole percent of the R groups in the molecule, R' represents an alkyl or aralkyl radical containing at least 8 carbon atoms, or the -R²COOH, -R²COOR⁺, or -R⁶OOCR⁶ group, wherein R², R³, and R⁶ are divalent hydrocarbon radicals and R⁴ and R⁶ are monovalent hydrocarbon radicals, A is R or R' with the proviso that A is R when x is equal to zero, x is an integer with a value of from zero to 50, y is an integer with a value of from 10 to 450, the sum of x and y is from 10 to 500 and the value of x is less than the value of y;

(B) from 0.5 to 50 weight parts of an extreme-pressure lubricant selected from sulfur-containing organic compounds, halogen-containing organic compounds, and phosphorus-containing organic compounds, and wherein said emulsion contains an amount of an emulsifying agent sufficient to stabilize said emulsified phase.

2. A composition according to claim 1 where R is selected from the group consisting of alkyl containing 1 to 4 carbon atoms, phenyl and cyclohexyl; R², R³ and R⁶ represent alkyene radicals, the number of carbon atoms in R², the combination of R³ and R¹ and the combination of R⁶ and R⁹ is at least 10; the extreme pressure lubricant is selected from the group consisting of sulfurized oils and pastes, organic sulfides, thiocarbonates, chlorinated hydrocarbons, chlorinated carboxylic acid derivatives, perfluoroalkyl-containing hydrocarbon compounds, organic phosphates and organic phosphites; the concentration of said lubricant is from 0.5 to 50 parts by weight per 100 parts by weight of said polyorganosiloxane; and said emulsifying agent is selected from the group consisting of non-ionic, cationic and anionic surfactants.

3. A composition according to claim 2 where at least 50 percent of the hydrocarbon radicals represented by R are methyl and said composition contains from 1 to 20 parts by weight of said lubricant per 100 parts by weight of said polyorganosiloxane.
**DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document with indication, where appropriate, of relevant passages</th>
<th>Relevant to claim</th>
<th>CLASSIFICATION OF THE APPLICATION (Int. Cl.5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P,Y</td>
<td>DATABASE WPII&lt;br&gt;Week 9217,&lt;br&gt;Derwent Publications Ltd., London, GB;&lt;br&gt;AN 92-139047 [17]&lt;br&gt;&amp; JP-A-4 084 643 (TORAY DOW CORNING) 17&lt;br&gt;March 1992&lt;br&gt;* abstract *</td>
<td>1,2</td>
<td>B22C3/00&lt;br&gt;C10M173/02&lt;br&gt;C10N30/06</td>
</tr>
<tr>
<td>A</td>
<td>EP-A-0 147 760 (HITACHI, LTD.)&lt;br&gt;10 July 1985&lt;br&gt;* abstract <em>&lt;br&gt;</em> page 5, line 19 - page 6, line 25 *</td>
<td>1,2</td>
<td>TECHNICAL FIELDS&lt;br&gt;B22C&lt;br&gt;C10M&lt;br&gt;C10N</td>
</tr>
<tr>
<td>A</td>
<td>GB-A-964 685 (DU PONT DE NEMOURS AND COMPANY)&lt;br&gt;22 July 1964&lt;br&gt;* claims 5,10 *</td>
<td>1,2</td>
<td></td>
</tr>
</tbody>
</table>

The present search report has been drawn up for all claims.

<table>
<thead>
<tr>
<th>Place of search</th>
<th>Date of completion of the search</th>
<th>Examiner</th>
</tr>
</thead>
<tbody>
<tr>
<td>THE HAGUE</td>
<td>06 APRIL 1993</td>
<td>RIBA VILANOVA M.</td>
</tr>
</tbody>
</table>

**CATEGORY OF CITED DOCUMENTS**

- **X**: particularly relevant if taken alone
- **Y**: particularly relevant if combined with another document of the same category
- **A**: technological background
- **O**: non-written disclosure
- **P**: intermediate document
- **T**: theory or principle underlying the invention
- **E**: earlier patent document, but published on, or after the filing date
- **D**: document cited in the application
- **L**: document cited for other reasons
- **M**: member of the same patent family, corresponding document