**Title:** SILICONE MODIFIED POLYURETHANES

Silicone modified polyurethane compositions having low surface energy characteristics comprise a polyurethane matrix in which 1-30% of a silicone compound is dispersed. The low surface energy of surface coatings comprised of these silicone modified polyurethanes provides environmentally safe and effective means of managing the effects of marine growth on vessels and static marine structures by the formation of a fouling release surface which enables simple and effective removal of marine organisms without damage to the surface coating. Silicone modified polyurethanes according to the invention also provide a useful alternative to polyester gel coats in fibreglass reinforced plastic boats and the like.
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</table>
Silicone Modified Polyurethanes.

This invention relates to novel silicone modified polyurethanes. The silicone modified polyurethanes find particular use as coating compositions and especially as marine paints. The modified polyurethanes can also be moulded or cast to form a variety of articles or films. The silicone modified polyurethanes have low surface energy and thus have good anti-stick properties making them suitable for fouling release paint compositions and anti-graffiti paint compositions.

Protective coating compositions such as paints are ever increasing in their complexity due in part to the large variety of substrates which need to be coated. Diverse articles or structures such as public buildings, aircraft, and marine vessels often require regular painting to resist environmental attack and to provide an aesthetic appearance. With large buildings in particular, maintenance of the exterior surface is both expensive and time consuming and any reduction in the maintenance of a building (ie. cleaning or painting thereof) is a distinct advantage.

Management of surfaces exposed to a marine environment is a major problem insofar as the cost of management of marine growths are concerned. Between hull cleaning operations, marine growths contribute greatly to hull drag and increased fuel consumption. For static marine
structures, such as oil rigs, marine growths can contribute to corrosion problems.

Various attempts have been made to overcome the problems associated with marine growth as cleaning is both time consuming and expensive. One common method is to provide a paint comprising inorganic or organometallic compounds which exhibit controlled release properties from the surface of the paint thereby providing the painted surface with toxic properties. A serious disadvantage of this type of paint however, is that the inorganic or organometallic compounds are leached out of the paints into the water systems and can result in pollution of marine organisms and creatures as well as coastal or inland waters where a large number of boats are used.

The use of toxins to control the fouling of underwater structures by marine life is unacceptable. Alternative non-toxic low surface energy coatings have been developed and field trailed over the last decade. These coatings have proved successful as fouling release coatings, however their use to date has been limited because of difficulties with application, durability and resistance to abrasion.

The maintenance of painted surfaces such as the walls on buildings has also become an increasing problem due in part to the increased levels of pollution in the environment. An additional problem affecting the maintenance
of painted surfaces is vandalism in the form of graffiti. Graffiti on painted walls is normally carried out using aerosol paint cans, liquid paint, inks, felt pens or the like. By far the most common form of graffiti is using aerosol spray paint cans. Previously it has been difficult to remove such graffiti from painted surfaces as the aerosol paint is formulated to adhere strongly to most surfaces. To remove such graffiti it is necessary to either vigorously scrub the paint work with the aid of solvents or to repaint the whole surface, both of which are time consuming and expensive.

Yet another form of painted surface comprises particles of polytetrafluoroethylene ("TEFLON" (trade mark)) bound in a paint matrix to confer low friction qualities to a painted surface. Low friction surfaces may be desirable to reduce wear in pipes or conduits carrying fluids, in particular fluids with solids in suspension. Similarly, in the handling of particulate materials such as grains, powdered chemical material and the like, the inner surface of storage hoppers, silos, road and rail freight containers may be coated with a PTFE containing paint in an endeavour to improve the flow characteristics of the particulate material over the surface of the container.

Polymeric compositions containing anti-slip or anti-block agents are known in the art and are commonly used as mould release agents. Typically, the polymer composition
contains an amount of silicone oil which bleeds out from the composition to provide the mould release properties. The rate of bleeding of the silicone oil can be controlled by the viscosity of the oil. The silicone is not bound within the polymeric matrix and can migrate to the surface of the composition. While this is desirable for mould release properties, such "bleeding" of the silicone compound from the polymeric composition results in difficulty in an application of a protective or decorative surface finish to the moulded article. A further disadvantage with these compositions is that while the presence of the silicone compound at or near the surface of the polymer composition can confer flexibility and resistance to weathering, these properties are relatively short lived due to the continual "bleeding".

United States Patent 4,500,688 discloses a melt processable pseudo-interpenetrating network of silicones in thermoplastic matrices. The composition is formed from separate batches of thermoplastic pellets, one of which contains a vinyl siloxane complexed with a platinum catalyst and the other containing a silicone hydride composition. The interpenetrating network is formed by mixing and extruding the pellets in a suitable plastics extruder. There is no disclosure of the use of liquid components and the use of the components as coatings.

United States Patent No. 4,302,553 describes an interpenetrating network of chemically different crosslinking
polymers which do not react together. The structure is described as entangled macrocyclic polymeric chains.

The patent discloses the formation of a macrocyclic structure comprising poly (dimethylsiloxane) and poly (urethane-urea) wherein aqueous emulsions of cross-linked polyurethane and hydroxy terminated poly (dimethylsiloxane) are intermixed to form an homogeneous mixture with sulphur and zinc oxide as cross-linking agents and butylated bisphenol A as an antioxidant. The mixture is cured at elevated temperatures of around 120°C whereby cross-linking is effected by chain extension of the respective polyurethane and poly (dimethylsiloxane) polymers.

European patent application 329375 discloses a composition to control marine fouling. The composition includes a curable polyorganosiloxane, an agent capable of curing the polyorganosiloxane to an elastomer, a polyisocyanate and a polyol. The cured polymer composition has a low surface energy due to the polyorganosiloxane elastomer which provides a fouling release. The specification further states that the cured product generally consists of domains of polyurethane within a network of cross-linked polyorganosiloxane. The amount of polyurethane should not exceed 40% by weight as it is stated that above this value the composition will not give a sufficiently low surface energy to prevent marine fouling. It is therefore evident that the composition of European patent specification
329375 is directed to a urethane modified polysiloxane with the urethane as the minor component.

It has now been found surprisingly that silicone modified polyurethanes having low surface energy can be formed with a major amount of polyurethane and a minor amount of polysiloxane.

In one form the invention resides in a curable liquid silicone modified polyurethane comprising (a) a polyol, (b) a polyisocyanate or polyisothiocyanate, (c) a polysiloxane comprising silicone hydride groups and (d) an unsaturated polysiloxane, wherein the amount of (c) and (d) is between 1 to 30% by weight of the polyurethane.

In another form, the invention resides in a curable liquid silicone modified polyurethane comprising (a) a polyol, (b) a polyisocyanate or polyisothiocyanate, (c) 1-30% by weight of the polyurethane of a cross-linkable and unsaturated organosiloxane polymer comprising silicone hydride groups.

In yet another form, the invention resides in a method for forming curable liquid silicone modified polyurethanes comprising premixing the unsaturated polysiloxane and polysiloxane comprising silicone hydride groups, adding the mixture to the polyol, and adding the polyisocyanate or polyisothiocyanate.

The silicone modified polyurethanes can be blended with other resins or fillers to confer desirable properties
such as increased flexibility or strength to the silicone modified polyurethane. For example, pitch or tar can be incorporated into the silicone modified polyurethane compositions to provide increased flexibility and durability to the composition or coatings prepared therefrom.

The silicone modified polyurethanes can be cured by the addition of catalysts and/or heating. The choice of the catalysts varies depending on the type of component used. Typically, a metal catalyst such as \( \text{H}_2\text{PtCl}_6 \) is used to polymerise the polysiloxane components. Alternatively, free radical producing catalysts such as organic or inorganic peroxides can be used with the application of heat to generate free radicals. Polymerisation of the polyisocyanate or polyisothiocyanate component with a polyol is well known in the art, and can be catalysed by any suitable catalyst. Catalysts for this type of polymerisation comprise tertiary amines or metal salts or mixtures thereof. The type of catalysts and the conditions to react the isocyanate or isothiocyanate with the polyol will be well apparent to a person skilled in the art.

The platinum catalyst can conveniently be premixed with the unsaturated polysiloxane before addition to the remaining compounds although this is not essential. It is preferred that the platinum catalyst is not premixed with the polysiloxane comprising the silicone hydride groups. If a free radical catalyst is used, these can suitably be premixed
as described above however, additional care needs to be taken
that the catalyst does not decompose into free radicals
prematurely. If a catalyst is used to promote the reaction
between the polyisocyanate or polyisothiocyanate and the
polyol, it is preferred that this is added immediately prior
to curing.

The unsaturated polysiloxane is suitably selected
from ethylenically unsaturated components such as hexenyl or
from other terminally unsaturated groups, although other
forms of unsaturation are also envisaged. The remaining
substituents on the polysiloxane are preferably alkyl groups
and an especially preferred alkyl group is the methyl group.
However, it is also envisaged that groups such as aromatic
groups, long chain alkyl groups or cycloalkyl groups can
advantageously be used. A preferred unsaturated polysiloxane
is a vinyl end grouped polydimethylsiloxane.

The silicone hydride containing polysiloxane is
preferably a polymethylsiloxane containing a number of
silicone hydride groups along the backbone of the polymer.

It is also possible for the hydride and the
unsaturated group to be present on the same siloxane polymer
backbone.

Alternatively, it is also possible to employ a
"one-component" organosiloxane component. The organosiloxane
would be required to be capable of cross-linking preferably
in a non-condensation reaction in the presence of a catalyst.
The polyol component can be chosen from any compound comprising at least two hydroxy groups which are reactive to isocyanate or isothiocyanate groups. Suitable polyols include hydroxy (meth)acrylic acid, or esters thereof, polyesters, polyethers, polythioethers, polyacetals, polycarbonates, polyester-amides all of which contain at least two reactive hydroxy groups. Branched polyalkyls with ester and ether groups may also be used. These polyols may be provided with additional functionality such as amino, thiol, or carboxylic groups.

The polyisocyanate or polyisothiocyanate can include acyclic, cyclic, cycloaliphatic or aromatic compounds. Additionally the isocyanate or isothiocyanate can be provided with hetero atoms in addition to the isocyanate or isothiocyanate nitrogen, and can also include unsaturated isocyanate or isothiocyanate. Polyphenyl-polyethylenes polyisocyanate and polyisothiocyanate including carbodiimide, allophanate, isocyanurate, urethane, acylated urea, urea or biuret groups and polyisocyanate prepolymer or any mixtures of the above may be suitable for the invention.

The considered useful ratio of polysiloxane to polyurethane is between 1 - 30% by weight with a preferred ratio of about 10% by weight polysiloxane to polyurethane.

The silicone modified polyurethanes of the invention can be prepared by admixing the polysiloxane, polylol and polyisocyanate in any order. Thus, the
polyurethanes can be prepared by admixing the polysiloxane containing hydride groups, the unsaturated polysiloxane, the polyol and the polyisocyanate together in appropriate amounts. Alternatively, the polysiloxanes can be premixed and added to the polyol after which the polyisocyanate is added. In a further alternative method, one of the polysiloxane components can be premixed with the polyol while the other of the polysiloxane components can be premixed with the polyisocyanate or polyisothiocyanate and the two premixtures can be admixed together. In yet another method, the polysiloxanes can be premixed with the polyisocyanate and the polyol added thereto.

The polyurethane can be in the form of a single component prepolymer composition containing the polyol and polyisocyanate or in the form of a two component composition containing the polyol and polyisocyanate as separate components. In a similar manner, the polysiloxanes can be in the form of a single component prepolymer containing both siloxanes or a two component composition containing the polysiloxane comprising hydride groups and the unsaturated polysiloxane respectively. The polyurethane and polysiloxane can be admixed in any of the above manners, for instance, the two component polyurethane composition can be admixed with the single or two component polysiloxane or vice versa.

The invention will be more fully illustrated by
reference to the following examples and comparative examples.

The components of the compositions are identified as follows:

**DESMOPHEN 651** - A branched hydroxy containing polyester sold by BAYER AUSTRALIA LTD.

**DESMOPHEN A365** - A hydroxy containing polyacrylate sold by BAYER AUSTRALIA LTD.

**DESMOPHEN 670** - A slightly branched hydroxy containing polyester sold by BAYER AUSTRALIA LTD.

**DESMOPHEN 900U** - A branched hydroxy containing polyether sold by BAYER AUSTRALIA LTD.

**DESMOPHEN A160** - A hydroxy containing polyacrylate sold by BAYER AUSTRALIA LTD.

**DESMODUR N75** - An aliphatic polyisocyanate sold by BAYER AUSTRALIA LTD.

**DESMODUR L75** - An aromatic polyisocyanate sold by BAYER AUSTRALIA LTD.

**BRAMITE SILICONE 2018 PART A** - Unsaturated polysiloxane liquid sold by Bramite Limited

**BRAMITE SILICONE 2018 - PART B** - Polysiloxane liquid containing silicone hydride groups sold by Bramite Limited

**BRAMITE SILICONE 2155** - A reactive unsaturated silicone
having silicone hydride groups
manufactured by BRAMITE LIMITED.

Bramite Silicone 2063

A silicone oil having a viscosity
of 1000 centistokes

Sylgard 184 Part A
Unsaturated polysiloxane liquid
sold by Dow Corning.

Sylgard 184 Part B
Polysiloxane liquid containing
silicone hydride groups sold by Dow
Corning.

Silicone RTV615A
Liquid silicone rubber sold by the
General Electric Company.

Silicone RTV615B
Liquid silicone rubber sold by the
General Electric Company.

Modafloc Resin Modifier
A flow and levelling agent sold by
Monsanto Australia Ltd.

Byk P-104S
A wetting and dispersion agent sold
by Hattrick Australia Ltd.

Rutile R-HD2
A rutile pigment sold by Tioxide
Australia Pty Ltd.

Talc TS15
Hydrous Magnesium Silicate sold by
Commercial Minerals Ltd.

Blanc Fixe "N"-Sachtleben
A barium sulfate extender sold
by A Victor Leggo & Co Pty Ltd.

Castor Oil Hydrogenated
A vegetable oil sold by Harcros
CheMicals Pty Ltd.

Special Pitch No. 4
A pitch sold by The Swift Watts
**EXAMPLE 1**

<table>
<thead>
<tr>
<th>Component A</th>
<th>Parts (% weight)</th>
</tr>
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<tr>
<td>5 1. Desmophen 651 67% in a 1:1 mixture of methoxy propyl acetate and xylene</td>
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</tr>
<tr>
<td>2. Modaflow 5% in methoxy propylacetate</td>
<td>1</td>
</tr>
<tr>
<td>3. Byk P-104S</td>
<td>1</td>
</tr>
<tr>
<td>4. Rutile R-HD2</td>
<td>24</td>
</tr>
<tr>
<td>10 5. Solvent (equal ratios of methyl isobutyl ketone, methylethyl ketone, methoxy propyl acetate and toluene)</td>
<td>16</td>
</tr>
<tr>
<td>6. 10:1 ratio of Bramite 2018 part A (containing a Pt catalyst) and Bramite 2018 part B</td>
<td>8</td>
</tr>
</tbody>
</table>

**Component B**

Desmodur N75 75% in methoxy propylacetate 22

The unsaturated polysiloxane (Bramite 2018 part A) containing a platinum catalyst and the polysiloxane comprising silicone hydride groups (Bramite 2018 part B) are premixed in the specified ratio (10:1). The mixture is added to the remaining compounds of component A and is mixed for 3-10mins at ambient temperatures using low shear mixing. This mixture is left at ambient temperatures for 2-4 weeks or until the viscosity of the mixture no longer increases. Component B is added to the mixture, with stirring to form
the silicone modified polyurethanes.

The mixture can be applied to a surface and cured to form a coating. If necessary, a solvent mixture can be utilized as a thinning mixture to faciltate the formation of coating.

EXAMPLE 2

<table>
<thead>
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<th>Component A</th>
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<td>1. Desmophen A365 65% in a 3:1 ratio of butylacetate and Xylene</td>
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<tr>
<td>2. Modaflow 5% in methoxypropylacetate</td>
<td>1</td>
</tr>
<tr>
<td>3. Byk P-104S</td>
<td>1</td>
</tr>
<tr>
<td>4. Rutile R-HD2</td>
<td>24</td>
</tr>
<tr>
<td>5. Solvent - equal ratios of methoxy isobutyl ketone, methyl ethyl ketone, methyl propyl acetate and toluene</td>
<td>8</td>
</tr>
<tr>
<td>6. Bramite 2018 part A (containing a Pt catalyst) and Bramite 2018 part B in a 10:1 ratio</td>
<td>8</td>
</tr>
<tr>
<td>7. Bramite Silicone 2063</td>
<td>1</td>
</tr>
</tbody>
</table>

Component B

1. Desmodur N75 | 16 |

The method of example 1 is used with the exception that the addition of the Bramite Silicone 2063 fluid eliminates the requirement of leaving the mixture for 2-4 weeks and component B of the example can be immediately
added.

EXAMPLE 3

Component A                      Parts (% weight)

5 1. Desmophen A365 65% in 3:1 ratio of butylacetate/Xylene 40
2. Desmophen 670 1
3. Modaflow 5% in methoxy propyl acetate 1
4. Byk P-104S 1
10 5. Rutile R-HD2 24
6. Solvent-equal ratios of methyl isobutyl ketone, methyl ethyl ketone, methoxy propyl acetate and toluene 8
7. 10:1 ratio of Bramite 2018 part A (containing a Pt catalyst) and Bramite 2018 part B. 8
15 8. Bramite Silicon 2063 1

Component B

Desmodur N75 - 75% in methoxy propyl acetate 16

The method of example 2 is used to form the silicone modified polyurethanes.

EXAMPLE 4

Component A                      Parts (% weight)

25 1. Desmophen 900U 22
2. Rutile R-HD2 22
3. Solvent - equal ratios of methoxypropyl acetate
methyl isobutyl ketone, and methylethyl ketone 24

4. Silicone RTV615A (containing a Pt catalyst)
and Silicone RTV615B in a 10:1 ratio 10

5 Component B
1. Desmodur L75 - 75% in ethyl acetate. 22

The components are reacted using the method of
example 1.

10

EXAMPLE 5

Component A Parts (% weight)

1. Desmophen 900U 14
2. Byk P-104S 1
3. Special Pitch No. 4 20

4. Talc TS15 4
5. Blanc Fixe "N" - Sachtleben 16
6. Castor oil Hydrogenated 2
7. Solvent - equal ratios of methyl isobutyl ketone,
methyl ethyl ketone and methoxy propyl acetate 15

8. Sylgard 184 part A (containing a Pt catalyst)
and Sylgard 184 part B 10:1 ratio 7

Component B

1. Desmodur L75, 75% in ethyl acetate 19

2. Toluene 2

The components are reacted using the method of
**EXAMPLE 6**

<table>
<thead>
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<th>Component A</th>
<th>Parts (% weight)</th>
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<tr>
<td>1. Desmophen A160 60% in Xylene</td>
<td>44</td>
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<tr>
<td>2. Rutile R-HD2</td>
<td>24</td>
</tr>
<tr>
<td>3. Solvent 2:1 ratio of Xylene and methoxy propyl</td>
<td></td>
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<tr>
<td>acetate</td>
<td>12</td>
</tr>
<tr>
<td>4. Bramite 2018 Part A (containing Pt catalyst)</td>
<td></td>
</tr>
<tr>
<td>and Bramite 2018 part B in a 10:1 ratio</td>
<td>4</td>
</tr>
<tr>
<td>Component B</td>
<td></td>
</tr>
<tr>
<td>1. Desmodur N75</td>
<td>10</td>
</tr>
<tr>
<td>2. Toluene</td>
<td>6</td>
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</tbody>
</table>

The components are reacted using the method of example 1.

**EXAMPLE 7**

<table>
<thead>
<tr>
<th>Component A</th>
<th>Parts (% weight)</th>
</tr>
</thead>
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<tr>
<td>20</td>
<td></td>
</tr>
<tr>
<td>1. Desmophen A365 - 65% in butyl acetate/Xylene</td>
<td>39</td>
</tr>
<tr>
<td>2. Rutile R-HD2</td>
<td>24</td>
</tr>
<tr>
<td>3. Solvent-equal parts of methyl isobutyl ketone,</td>
<td></td>
</tr>
<tr>
<td>methyl ethyl ketone, Toluene and ethyl glycol</td>
<td></td>
</tr>
<tr>
<td>acetate</td>
<td>15</td>
</tr>
<tr>
<td>25 4. Silicone - Bramite Silicone 2155</td>
<td>6</td>
</tr>
</tbody>
</table>
Component B

Desmodur N75 75% in methoxy propyl acetate 16

The compounds of component A were admixed and 50ppm (relative to the polysiloxane) of a platinum catalyst $\text{H}_2 \text{PtCl}_6$ was added. After stirring at ambient temperature for 3-10 minutes component B was added to give the silicone modified polyurethanes.

EXAMPLE 8

<table>
<thead>
<tr>
<th>Component A</th>
<th>Parts (% weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td></td>
</tr>
<tr>
<td>1. Desmophen A160 60% in Xylene</td>
<td>44</td>
</tr>
<tr>
<td>2. Modaflow 5% in methoxy propyl acetate</td>
<td>1</td>
</tr>
<tr>
<td>3. Byk P-1045</td>
<td>1</td>
</tr>
<tr>
<td>4. Rutile R-HD2</td>
<td>24</td>
</tr>
<tr>
<td>5. Solvent 2:1 ratio of Xylene and methoxy propyl acetate</td>
<td>12</td>
</tr>
<tr>
<td>6. Silicone-Bramite Silicone 2155</td>
<td>4</td>
</tr>
</tbody>
</table>

Component B

1. Desmodur N75 10

2. Toluene 6

The components are reacted using the method of Example 7.

EXAMPLE 9

One pack moisture cured system

25 1. Desmodur N75 60 parts
2. Xylene 30 parts
3. Dibutyltin dilaurate 0.3 parts
4. Silicone RTV615A and
   Silicone RTV615B 10:1 ratio 9.7 parts
Admixture of the above compounds gave a one pack moisture
cured system.

**COMPARATIVE EXAMPLE 1**

This formulation is identical to example 1 without
the Bramite 2018 part A and Bramite 2018 part B. The solvent
component is increased to 24 parts.

**COMPARATIVE EXAMPLE 2**

This formulation is identical to example 2 without
the Bramite 2018 part A and Bramite 2018 part B and Bramite
Silicone 2063. The solvent component is increased to 16
parts.

It is believed that the Bramite Silicone 2063 can
be partially or totally substituted by polyphenylmethyl
siloxane fluids or fluorinated hydrocarbons with low surface
energy.

Other silicone elastomers such as RTV3110 (produced
by DOW CORNING as a two part mixture) can be used. These
silicones are catalysed by dibutyltin dilaurate or stannous
octanoate. Although the silicones are of high viscosity,
thinning with appropriate solvents can be carried out prior
to incorporation into the polyol.

The silicone modified polyurethanes can be formed
as a single component by inclusion of a polyurethane prepolymer which cures by reaction with atmospheric moisture. A suitable prepolymer is Desmodur E21 sold by BAYER AUSTRALIA LTD. Alternatively, a one component moisture cured silicone modified polyurethane can be formed based on an aliphatic polyisocyanate such as Desmodur N75.

Although the above examples have used hydroxy containing polyacrylates and other polyl compounds sold by BAYER AUSTRALIA, these compounds may be substituted by hydroxy containing polyacrylates from HOECHST AUSTRALIA LTD under the trade mark MACRYNAL SM series and hydroxy containing polyacrylates from CRAY VALLEY PRODUCTS LTD U.K. which are sold under the trade name SYNOCURE. Similarly, an aliphatic polyisocyanate designated as HARTBEN A75 sold by VICTOR LEGGO AND CO PTY LTD is considered a suitable alternative to Desmodur N75.

The silicone modified polyurethane system of example 3 containing a small percentage of Desmophen 670 has been used for coating a product sold by FERRO CORPORATION (AUST) PTY LTD under the trade name VULKEM which is used to provide a very flexible substrate on pools.

The silicone modified polyurethane compositions of example 5 incorporating the pitch provides heavy duty coatings with improved weathering properties in terms of gloss retention. Polyurethane pitch or tar formulations not including silicone modification suffer from loss of gloss
within six months of exposure.

The silicone modified polyurethanes of the examples can be unpigmented and these formulations usually have UV stabilizers present as well as the levelling agent MODAFLOW. Suitable stabilizers include Tinuvin 292 and Tinuvin 900 (trade mark CIBA-GEIGY AUSTRALIA LTD) as a 10% solution in xylene and which are added in two parts and four parts respectively to the formulation.

An alternative method of forming the silicone modified polyurethane compositions of the examples is to premix the polyl and polyisocyanate or polyisothiocyanate at ambient temperature together with the desired solvent mixture and additives using low shear mixing conditions. The unsaturated polysiloxane (containing platinum catalyst) and the polysiloxane containing silicone hydride groups are premixed and then added to the polyl/isocyanate or isothiocyanate mixture over a period of 3-10 minutes at ambient temperatures and using low shear mixing conditions. This mixture can be applied to a substrate in the form of a coating to cure at room temperature.

Table 1 lists various properties of certain of the exemplified silicone modified polyurethanes compared with identical polyurethanes not containing silicone. Unless otherwise specified, the silicone modified polyurethane coatings have been tested to Australian Standards 2602-Paints for steel structures: full gloss polyurethanes. The
tests were carried out in accordance with Australian Standards 1580 - Methods of Test for Paints and Related Materials.

Although the silicone polymers prepared by Bramite Limited, Dow Corning and General Electric for use in the examples above are generally similar in properties, the polymers manufactured by Bramite Limited are preferred in practice.
<table>
<thead>
<tr>
<th>PROPERTY</th>
<th>TEST METHOD</th>
<th>COMPARATIVE EXAMPLE 1</th>
<th>EXAMPLE 1</th>
<th>COMPARATIVE EXAMPLE 2</th>
<th>EXAMPLE 2</th>
<th>EXAMPLE 3</th>
<th>EXAMPLE 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Application Properties</td>
<td>AS1580-205.1, 205.2, 205.3</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td></td>
<td></td>
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<tr>
<td>2. Pot life (% change)</td>
<td>AS1580-214.2&lt;sup&gt;1&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
<td>&lt;10</td>
<td>&lt;10</td>
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<tr>
<td>3. Surface dry</td>
<td>AS1580-401.1</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. Bend test</td>
<td>AS1580-402.1</td>
<td>P</td>
<td>F</td>
<td>P</td>
<td>P</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5. Scratch resistance (kg)</td>
<td>AS1580-403.1</td>
<td>&gt;2.1</td>
<td>&gt;2.0</td>
<td>&gt;2.1</td>
<td>&gt;2.1</td>
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<tr>
<td>6. Adhesion (knife test)</td>
<td>AS1580-408.2</td>
<td>4</td>
<td>4</td>
<td>4</td>
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<tr>
<td>7. Recoating properties&lt;sup&gt;2&lt;/sup&gt;</td>
<td>AS1580-402.1</td>
<td>P</td>
<td>P</td>
<td>P</td>
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<tr>
<td></td>
<td>AS1580-403.1</td>
<td>&gt;2.1</td>
<td>&gt;2.1</td>
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<tr>
<td></td>
<td>AS1580-408.2</td>
<td>4</td>
<td>4</td>
<td>4</td>
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<tr>
<td>8. Overcoating properties&lt;sup&gt;3&lt;/sup&gt;</td>
<td>AS1580-402.1</td>
<td>F</td>
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<td></td>
<td>AS1580-403.1</td>
<td>0.65</td>
<td>0.35</td>
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<tr>
<td></td>
<td>AS1580-408.2</td>
<td>3</td>
<td>2</td>
<td>3</td>
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<tr>
<td>PROPERTY</td>
<td>TEST METHOD</td>
<td>COMPARATIVE EXAMPLE 1</td>
<td>EXAMPLE 1</td>
<td>COMPARATIVE EXAMPLE 2</td>
<td>EXAMPLE 2</td>
<td>EXAMPLE 3</td>
<td>EXAMPLE 4</td>
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<tr>
<td>9. Taber abrasion resistance (weight loss in mg) (CS17, 1000g, 500 cycles)</td>
<td>ASTM D4060</td>
<td>33</td>
<td>31</td>
<td>38</td>
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<tr>
<td>10. Coefficient of friction (μ)</td>
<td>ASTM D4518</td>
<td>0.11</td>
<td>0.04</td>
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<td>11. Gloss (60° exposure head)</td>
<td>AS1580-602.2</td>
<td>92</td>
<td>90</td>
<td>89</td>
<td>94</td>
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<td>12. Durability (atmospheric weathering): 12 months</td>
<td>AS1580-457.1</td>
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<tr>
<td>- assessment of individual defects</td>
<td>AS1580-481.1</td>
<td>10</td>
<td>10</td>
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<td>- colour change (ΔE)</td>
<td>AS1580-601.2</td>
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<td>- gloss</td>
<td>AS1580-602.2</td>
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<td>90</td>
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<td>- assessment of individual defects</td>
<td>AS1580-481.1</td>
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<td>- colour change (ΔE)</td>
<td>AS1580-601.2</td>
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<td>1.4</td>
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<td>- gloss</td>
<td>AS1580-602.2</td>
<td>39</td>
<td>28</td>
<td>26</td>
<td>35</td>
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<tr>
<td>PROPERTY</td>
<td>TEST METHOD</td>
<td>COMPARATIVE EXAMPLE 1</td>
<td>EXAMPLE 1</td>
<td>COMPARATIVE EXAMPLE 2</td>
<td>EXAMPLE 2</td>
<td>EXAMPLE 3</td>
<td>EXAMPLE 8</td>
</tr>
<tr>
<td>----------------------------------------------</td>
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<td>------------------------</td>
<td>-----------</td>
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<tr>
<td>14. Surface drag (pressure drop:mm Hg)</td>
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<td>-</td>
<td>-</td>
<td>98</td>
<td>96</td>
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<td>15. Water resistance</td>
<td>AS1838</td>
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<td>-</td>
<td>6B</td>
<td>8A</td>
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<td>- assessment of blistering</td>
<td>AS1580-481.2</td>
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<tr>
<td>16. Durability and resistance to fouling</td>
<td>AS1580-481.5</td>
<td>-</td>
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<td>- assessment of individual defects</td>
<td>AS1580-481.1</td>
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<td>17. Tensile strength (MPa) (Die C)</td>
<td>ASTM D412</td>
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<td>19.1</td>
<td>14.2</td>
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<td>18. Elongation % (Die C)</td>
<td>ASTM D412</td>
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<td>-</td>
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<td>19. Tear Strength (N/mm) (Die C)</td>
<td>ASTM D624</td>
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<td>17.1</td>
<td>13.2</td>
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<td>20. Surface profile</td>
<td>-</td>
<td>0.3</td>
<td>0.8</td>
<td>0.5</td>
<td>0.8</td>
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<tr>
<td>- centre line average (um)</td>
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<td>21. Durability (Atlas Weatherometer accelarated weathering) : 1,000 hours UV</td>
<td>-</td>
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<tr>
<td>- assessment of gloss</td>
<td>AS1580.481.1</td>
<td>-</td>
<td>-</td>
<td>7</td>
<td>9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
NOTES - TABLE 1

(1) AS2602 requires testing to AS1580-214.1.

(2) AS2602 requires testing within 24 hours of application of second coating. This was extended to 7 days "normal" curing, the 24 hour cure time being insufficient.

(3) Using a black enamel paint that might commonly be used for graffiti purposes. Tested after 7 days.

1. **Application properties**

Modified coatings can be applied by brushing, conventional air spraying and roller coating without any evidence of film defects. The presence of the silicone aids the flow, spreading, levelling and lapping properties compared to the unmodified coating.

2. **Pot life**

This test was carried out according to AS1580-214.2 (consistency - Flow Cup) following the procedure outlined in AS2602. Both the silicone modified polyurethane and the polyurethane coatings were thinned using spraying thinners, so as to give a flow time of 22 seconds. After a period of 3 hours at 25°C, flow time was measured at 23-24 seconds for both the silicone modified polyurethanes and the unmodified polyurethanes. The results indicate suitability of both systems with respect to pot life and indirectly suggests minimal, if any, reaction between the silicone and
polyurethane components.

3. **Surface dry**

This test indicates minimal difference between the silicone modified and unmodified polyurethanes. Indirectly this suggests some degree of curing of the silicone has occurred prior to addition of polyisocyanate component.

4. **Bend test**

This test is considered an indication of flexibility and adhesion of the coatings.

5. **Scratch resistance**

The curing properties of the polyurethanes is assessed by measuring the scratch resistance; the film having cured for 7 days in accordance with AS1580-403.1 should withstand a load of 1.5kg. The scratch resistance of the product of Example 1 is slightly down from all other coatings trialled.

6. **Adhesion (knife test)**

Due to the problem of adherence of pressure-sensitive tape over cuts made in the film (see AS1580-408.4 Adhesion-cross cut) the knife test method was used. A rating of 4 represents trace peelings or removal along incisions, in other words, adhesion to the substrate is very good.

7. **Recoating properties**

A standard cure period of 7 days was used. Results clearly show the ability of the silicone modified polyurethanes to be recoated.
8. **Overcoating properties**
A variation of 7 above was used to examine the effect of applying a black enamel paint that might be used by graffiti artists. Results clearly demonstrate the inability of the black enamel to form a strong chemical bond with the silicone modified polyurethane coatings. The enamel film, when applied to the silicone modified polyurethane coatings, showed considerable film defects due to fish-eyeing, etc.

9. **Abrasion resistance**
The abrasion resistance of all the coatings was excellent.

10. **Coefficient of friction**
The test method used is a variation of ASTM D4581 in that a 500gm vertical load was placed on each coated coupon through a 9.5mm diameter steel ball. The coated coupon sample was mounted on a flat steel plate that could advance on low friction bearings. The plate was pulled forward at a speed of 50mm/minute by the cross-head of a JJ Lloyd testing machine by means of a nylon cord. The force required to propel the plate was measured by means of a load cell. Results clearly show a significant reduction in surface friction coefficient of the silicone modified polyurethane coatings.

11. **Gloss (60° exposure head)**
Specular gloss was measured for those samples prepared for accelerated QUV weathering. All coatings met the minimum
requirement of AS2602, in that specular gloss shall not be less than 85 gloss units.

12. **Durability**

After a weathering period of 12 months, property defects such as erosion, cracking, checking, flaking and peeling, delamination, rusting with blisters, rusting and blistering were not observed and the highest rating of 10 was noted. These results are to be expected and the minimum requirement of AS2602 is that a rating of 10 be attained during the first 48 months. Results do show that no adverse effects are noted for the silicone modified polyurethane systems.

13. **Durability (QUV accelerated weathering - 800 hours)**

The coatings were subjected to accelerated weathering using a fluorescent ultraviolet (UV) and condensation apparatus to simulate the deterioration caused by sunlight and water as rain or dew. Repeated cycles of 4hrs UV light followed by 4hrs condensation were used. Results indicate that the silicone modified polyurethane of examples 2, 3 and 8 perform better, in terms of gloss retention than Comparative Example 2 or Example 1.

14. **Surface drag**

The interior surface of PVC pipes of 6 metres in length, 50mm in diameter, were coated with the product of Comparative Example 2 and of Example 2. One pipe was left uncoated. Pressure drop was measured over a 5 metre distance, velocity of the water being measured at 4.0m/s, nominal flow being
7.34 kg/s. Pressure drop for the PVC pipe was 100mm Hg. Results have been corrected to a diameter of 50.0 mm. Results suggest that the silicone modified polyurethane coating will also effect a reduction in drag for sailing vessels and other marine craft, not to mention improving the efficiency of pumping systems, etc.

15. **Water resistance**

In this test, the effectiveness of the silicone-modified polyurethane coating of Example 2 in improving the water resistance rating (with respect to blistering) of a gel-coated laminate was ascertained. The procedure differed to AS1838 in that a temperature of 65°C was maintained for 300 hours and not 100°C for 100 hours. The gel-coat laminate was known to have a degradation rating of 5 or, as assessed by AS1580-481.2, a rating of 4C. The silicone modified polyurethane coating significantly improved the blister rating of the gel-coat and showed an improvement with respect to the polyurethane system of the Comparative Examples. It should be noted that there was no sign of blistering or any other film defect when coatings were applied to polyester DMC (dough moulded compound) panels. Results indicate improved water resistance of the silicone modified coating and suggests that the application of such coatings to fibreglass vessels will provide increased protection with respect to osmosis.

16. **Durability and resistance to fouling in water**
These tests were carried out in an area of heavy fouling activity and where temperature of the water remains temperate. Unmodified polyurethane and silicone modified polyurethane test panels allowed to sit in this environment for a total of 12 months, show fouling very much to the same degree. The silicone modified urethane coatings are nontoxic and will therefore foul. However, on cleaning the test panels it is observed that the silicone modified polyurethane coatings are easily cleaned with no evidence of individual defects whereas the unmodified coatings are quite difficult to clean and, where barnacles have been present, damage to the coating occurs.

17. **Tensile strength**

Results were obtained after plaques were prepared approximately 1mm thick.

18. **Elongation**

Results indicate an increase in flexibility of the silicone modified polyurethane. These values can be compared with an unpigmented silicone elastomer (110%), the unpigmented polyurethanes of Comparative Examples 1 or 2 (59%) and the unpigmented silicone modified polyurethanes of Examples 1, 2, 3 and 8 (66%).
19. **Tear strength**

Results indicate a decrease in tear strength for the silicone modified polyurethanes. These results can be compared with an unpigmented silicone elastomer (6.7), the unpigmented polyurethanes of Comparative Examples 1 or 2 (12.8) and the unpigmented silicone modified polyurethanes of Examples 1, 2, 3 and 8 (11.5).

20. **Surface profile**

Tests carried out on coatings sprayed under optimum conditions with respect to thinning of paint system. Surface texture was assessed using a Taylor Hobson Talysurf measuring device which draws a stylus needle over a measured length of coating.

21. **Durability (Atlas Weatherometer accelerated weathering - 1,000 hours uv)**

Results indicate an improvement in gloss retention of the silicone modified polyurethanes.

Particularly advantageous properties of coatings prepared from the silicone modified polyurethanes of the examples are listed below:

<table>
<thead>
<tr>
<th>EXAMPLE</th>
<th>PROPERTIES</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Good light stability; gloss retention; outdoor resistance, and chemical resistance.</td>
</tr>
<tr>
<td>2</td>
<td>Excellent fouling release properties when used as a marine paint.</td>
</tr>
</tbody>
</table>
Excellent fouling release properties, good flexibility.

Good fouling release properties and anti-corrosion properties.

Excellent industrial coatings, heavy duty marine coatings.

Good resistance to weathering, water, detergent solutions and chemicals.

Rapid air drying finish, good weather resistance, light stability, solvent and petrol resistance.

A particular advantage of the coatings of the examples resides in their low surface energy properties.

Advantage is taken of these low surface energy properties in the use of silicone modified polyurethane compositions as a means of effectively and safely managing the effects of marine growth on vessels such as commercial ships, pleasure craft, ferries and the like as well as static marine structures such as oil rigs, jetty piles, etc.

Although these silicone modified polyurethane compounds are inherently non toxic to marine organisms and otherwise preserve the integrity of the marine environment, their low surface energy characteristics provide a fouling release coating which inhibits the degree of adhesion of
marine organisms. This in turn permits simple and inexpensive underwater cleaning operations to be carried out or otherwise less time consuming slipping of vessels for removal of marine growth. The fouling release coatings enable ready removal of marine growth by less rigorous scrubbing or high pressure hosing without damaging the coating surface. Few organic substances will bond strongly to the surface of the coatings and thus the coating can be used as anti-graffiti coatings on buildings, railway carriages or other surfaces likely to be disfigured by graffiti artists. In addition they may be used as fouling release coatings on marine vessels. Dirt pick up is reduced and therefore surface tracking is also reduced. When used as a decorative and/or protective coating on buildings, the coatings have a low coefficient of friction and together with the reduced adhesion of dirt of other particles the coating is easily cleansed by rain or washing.

The coatings are more flexible and softer than conventional cross-linked paint coatings and thus exhibits improved scratch resistance.

The coatings while having an anti-stick surface can be recoated with a second coat having good adhesion properties to the first coat. Thus, it is not necessary to strip the first coat. Further, the coatings can be applied directly to a substrate without requiring primer coats or "tie" coats.
In an endeavour to ascertain the physical structure of the silicone modified polyurethane compositions, a number of tests were carried out. These tests included:

**Pyrolysis/Gas Chromatography** Tests conducted on both modified and unmodified polyurethane systems suggest that no interaction occurs between the urethane and silicone component. The modified system showed no peaks associated with the silicone component and this was considered to be a most unusual result. Polyurethane traces in both cases were identical.

**Thermal Analysis** Thermal analysis using a differential spectral calorimeter showed that the glass transition state (Tg) of the silicone elastomer, the modified and the unmodified urethane acrylic compositions were substantially identical.

**Physical Tests** Tensile elongation and tear strength measurements all showed reduced values for silicone modified systems.

While not wishing to be bound by speculation, investigations suggest that the silicone modified polyurethanes of the invention comprise domains of at least partially cured polysiloxanes within a network of polyurethane. It is possible that an amount of inter-penetration and/or chemical bonding occurs along the interface between the silicone domains and the polyurethane.
However, it is also possible that some degree of chemical coupling occurs between the silicone and polyurethane to give cross-linked, and/or graft polymers or block polymers.

It is also possible that the polyol may react with a silicone hydride functionality to link at least a portion of the polyurethane resin to the polysiloxane domains. The silicone hydride containing polysiloxane may react with a polyol to form polar segments which may aggregate into micelle-like particles with silicone polymer chains extending into the surrounding polyurethane matrix.

It is also considered that the respective densities and polarities of the polysiloxanes and the polyol may have a profound bearing on the type of product formed. The polysiloxanes typically have a low solubility in the polyol/solvent mixture and thus tend to form an emulsion or colloidal suspension of fine droplets of the silicone in the polyol upon mixing. The hydroxy containing polyacrylates (eg. Desmophen A365) can form an emulsion with the unsaturated polysiloxane (eg. Bramite 2018 Part A) and silicone hydride containing polysiloxane (eg. Bramite 2018 part B) which is stable for a period of about three weeks after which time appreciable phase separation had occurred. In this example it was observed that the density of the polysiloxanes and solvents approximated the density of the polyol and it is believed that this contributes to the stability of the emulsion. Addition of additives such as
pigments appear also to inhibit phase separation.

As the polyurethane system comprises a polyol with a number of hydroxyl groups which normally react with the isocyanate groups, it is possible that some of these hydroxyl groups react with hydrosilane functional groups to chemically bond the silicone domains within the polyurethane matrix. Alternatively, these could be formed as polymer chains having a polyurethane function at one end and a silicone function at the other. A further postulation is that through inhibition of polymerisation of the silicone monomers, the proportion of uncross-linked silicone monomer may be free to migrate through the polyurethane matrix. That being the case, it is likely through surface tension effects, that there occurs a greater concentration of silicone monomers near the exposed surface of the polyurethane matrix. This concentration may then allow cross-linking of the silicone monomers in an interpenetrating network as steric inhibition is reduced.

Although there is no definite evidence to support any particular postulation of the molecular structure of the silicone modified polyurethane systems according to the invention, the most likely structure is believed to comprise micelle-like domains of silicone polymer with silicone chains extending into the surrounding polyurethane matrix. These extended silicone chains probably bind to the polyurethane matrix by a combination of chemical bonding between silicone hydride and the polyol hydroxy groups as
well as interpenetration of the polyurethane molecules.

The silicone modified polyurethane compositions according to the invention may have application in a wide range of fields. The silicone modified polyurethanes have particular application as non-toxic environmentally safe fouling release coatings for marine applications including all manners of marine vessels and marine structures such as oil rigs and the like.

Heavy duty coatings comprising pitch or tar may be used as anti-corrosion coatings in marine and land based structures particularly where marine fouling release properties are required.

Other applications include enhanced slip coatings for containers of particulate materials such as grains, cement powders, and sticky substances such as sugar and molasses and where non-toxic low friction coatings are required. Such non-toxic low friction coatings are also suitable for the interior of pipes and other conduits. These non-toxic coatings could be used for example in the pumping of town water or in the food industry such as in conveyancing of beverages. In other applications such as the pumping of cooling water in condensers of power stations, substantial improvement in pump efficiency by reduction of head losses can be expected.

Application of the silicone modified polyurethane coatings according to the invention in aeronautic
applications is expected to lead to increased fuel savings due to reduced air drag on aeroplanes and the like.

A particularly advantageous application of the silicone modified polyurethane compositions is in the manufacture of fibreglass (FRP) products such as boats. As an alternative to conventional polyester gel coats, compositions according to the invention provide a means of overcoming, many of the traditional gel coat problems such as cracking, blistering, osmosis and water absorption. The greater flexibility and improved resistance to moisture absorption impart improved impact resistance, resistance to abrasion which otherwise in more brittle polyester gel coats leads to "star" cracking which in turn allows water to penetrate the gel coat/fibreglass structure, often with disastrous effects. At the same time, the low surface energy of the compositions provides an environmentally sound, non-toxic fouling release surface for above and below water surfaces.

In yet further modifications of the invention there are provided mouldable or castable silicone modified polyurethane compositions applicable in the field of medicine, such as surgical prostheses, or in other fields such as automotive components, cast films, polymeric laminates for automotive and domestic upholstery and the like.

It should be appreciated that various other changes
and modifications may be made to the examples without departing from the spirit and scope of the invention as defined in the appended claims.
CLAIMS:
1. A curable liquid silicone modified polyurethane composition comprising (a) a polyol, (b) a polyisocyanate or polyisothiocyanate (c) a polysiloxane comprising silicone hydride groups, and (d) an unsaturated polysiloxane, wherein the amount of (c) and (d) is between 1-30% by weight of the polyurethane.
2. The composition as claimed in claim 1, wherein the amount of (c) and (d) is between 5-15%.
3. The composition as claimed in claim 2, wherein the amount of (c) and (d) is about 10%.
4. The composition as claimed in claim 1, wherein the amount of said polyol is between 10-60%.
5. The composition as claimed in claim 1, wherein the amount of said polyisocyanate or polyisothiocyanate is between 10-20%.
6. The composition as claimed in claim 1, wherein the ratio of (c) to (d) is between 8:1 to 12:1.
7. The composition as claimed in claim 6, wherein the ratio of (c) to (d) is about 10:1.
8. The composition as claimed in claim 1, wherein said polyol is selected from hydroxy containing polyesters, hydroxy containing polyacrylates and hydroxy containing polyethers.
9. The composition as claimed in claim 1, wherein said polysiloxane comprising silicone hydride groups comprises one
or more of said silicone hydride groups.

10. The composition as claimed in claim 1, wherein said unsaturated polysiloxane comprises one or more vinyl groups.

11. The composition as claimed in claim 1, wherein said polyisocyanate of polyisothiocyanate is selected from aliphatic or aromatic polyisocyanates or polyisothiocyanates.

12. A method of forming a curable liquid silicone modified polyurethane composition as claimed in claim 1, comprising the steps of mixing said polysiloxane comprising silicone hydride groups, said unsaturated polysiloxane and said polyol as a first component and adding said polyisocyanate or polyisothiocyanate as a second component to said first component.

13. A method of forming a curable liquid silicone modified polyurethane composition as claimed in claim 1, comprising the steps of mixing said polysiloxane comprising silicone hydride groups, said unsaturated polysiloxane and said polyisocyanate or polyisothiocyanate as a first component and adding said polyol as a second component to said first component.

14. A method of forming a curable liquid silicone modified polyurethane composition as claimed in claim 1, comprising the steps of mixing said polyol, said polyisocyanate or polyisothiocyanate, said polysiloxane comprising silicone hydride groups and said unsaturated polysiloxane as separate components.
15. A method of forming a curable liquid silicone modified polyurethane composition as claimed in claim 1, comprising the steps of mixing said polyol and said polyisocyanate or polyisothiocyanate as a first component, mixing said polysiloxane comprising silicone hydride groups and said unsaturated polysiloxane as a second component and admixing said components.

16. A method of forming a curable liquid silicone modified polyurethane composition as claimed in claim 1, comprising the steps of mixing said polyol, said polyisocyanate or polyisothiocyanate and said polysiloxane comprising silicone hydride groups as a first component and adding said unsaturated polysiloxane as a second component to said first component.

17. A method of forming a curable liquid silicone modified polyurethane composition as claimed in claim 1, comprising the steps of mixing said polyol, said polyisocyanate or polyisothiocyanate and said unsaturated polysiloxane as a first component and adding said polysiloxane comprising silicone hydride groups as a second component to said first component.

18. A method of forming a curable liquid silicone modified polyurethane composition as claimed in claim 1, comprising the steps of mixing said polyol and said polysiloxane comprising silicone hydride groups as a first component, mixing said polyisocyanate or polyisothiocyanate
as a second component and admixing said components.

19. A method of forming a curable liquid silicone modified polyurethane composition as claimed in claim 1, comprising the steps of mixing said polyol and said unsaturated polysiloxane as a first component, mixing said polyisocyanate or polyisothiocyanate as a second component and admixing said components.

20. The composition as claimed in claim 1, comprising 1-25% of a reinforcing agent.

21. The composition as claimed in claim 20, wherein said reinforcing agent is selected from particulate fillers, fibrous fillers and cross-linkable polymeric materials.

22. A coating composition comprising the composition as claimed in claim 1.

23. A non-toxic fouling release composition for coating surfaces exposed to a marine environment comprising the composition as claimed in claim 1.


25. An anti-graffiti coating comprising the composition as claimed in claim 1.

26. A moulded article comprising the composition as claimed in claim 1.

27. A cast sheet-like material or laminate comprising the composition as claimed in claim 1.
I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) 6

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl. 4 CO8G 18/61, 18/62, 18/83; C09D 3/72, 3/82, 5/14; C09K 3/14; B32B 27/40

II. FIELDS SEARCHED

Minimum Documentation Searched 7

<table>
<thead>
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<th>Classification System</th>
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Documentation Searched other than Minimum Documentation to the extent that such documents are Included in the Fields Searched 8

AU: CO8G 18/61, 18/62, 18/83

III. DOCUMENTS CONSIDERED TO BE RELEVANT 9

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<tr>
<th>Category*</th>
<th>Citation of Document, with indication, where appropriate, of the relevant passages</th>
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<tr>
<td>X</td>
<td>DERNENT ABSTRACT ACCESSION NO. 035455/43, Class G02, JF,A, 57-172917 (KANEGAFUCHI CHEM KK) 25 October 1982 (25.10.82)</td>
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<tr>
<td>A</td>
<td>DERNENT SOVIET INVENTIONS ILLUSTRATED SECTION I, CHEMICAL, issued February 1971, Plastics, Metal Finishing P.3, SU 262385 (POLIMER CHEMISTRY INST., ACAD. SCIE. UKR. SSR) 14 October 1970 (14.10.70)</td>
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* Special categories of cited documents: 10

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

IV. CERTIFICATION

Date of the Actual Completion of the International Search 6 April 1990 (06.04.90)
International Searching Authority Australian Patent Office

Date of Mailing of this International Search Report 12 APRIL 1990
Signature of Authorized Officer P. SEIN

Form PCT/ISA/210 (second sheet) (January 1985)