



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification<sup>4</sup> : <b>C09K 5/00</b></p>	<p><b>A1</b></p>	<p>(11) International Publication Number:      <b>WO 85/ 03719</b> (43) International Publication Date:   29 August 1985 (29.08.85)</p>
<p>(21) International Application Number:   PCT/GB85/00060 (22) International Filing Date:   14 February 1985 (14.02.85) (31) Priority Application Number:           8404208 (32) Priority Date:                   17 February 1984 (17.02.84) (33) Priority Country:                        GB  (71) Applicant (<i>for JP only</i>): BP CHEMICALS LIMITED [GB/GB]; Belgrave House, 76 Buckingham Palace Road, London SW1W OSU (GB).  (72) Inventor; and (75) Inventor/Applicant (<i>for US only</i>) : GRITTI, Serjio [IT/ CH]; 50, chemin d'Ecojio, CH-1290 Versoix/Geneva (CH).</p>		<p>(74) Agent: HARRY, John; BP International Limited, Pa- tents Division, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN (GB).  (81) Designated States: JP, US.  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: STABILISERS FOR SILICATES IN ANTIFREEZE COMPOSITIONS</p> <p>(57) Abstract</p> <p>Stabilizers for silicate corrosion inhibitors useful in polyalkylene antifreeze compositions are provided comprising an organosiloxane containing a polyoxyalkylene end chain.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GA	Gabon	MR	Mauritania
AU	Australia	GB	United Kingdom	MW	Malawi
BB	Barbados	HU	Hungary	NL	Netherlands
BE	Belgium	IT	Italy	NO	Norway
BG	Bulgaria	JP	Japan	RO	Romania
BR	Brazil	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	LI	Liechtenstein	SN	Senegal
CH	Switzerland	LK	Sri Lanka	SU	Soviet Union
CM	Cameroon	LU	Luxembourg	TD	Chad
DE	Germany, Federal Republic of	MC	Monaco	TG	Togo
DK	Denmark	MG	Madagascar	US	United States of America
FI	Finland	ML	Mali		
FR	France				

STABILISERS FOR SILICATES IN ANTIFREEZE COMPOSITIONS

The present invention relates to stabilizers for silicates used in antifreeze compositions, and in particular, for antifreeze compositions based on alkylene glycols.

It is known that alkali metal silicates are effective corrosion inhibitors for metal alloys, e.g. aluminium alloys. It has therefore been desirable to use alkali metal silicates in antifreeze formulations. However, alkali metal silicates tend to form gels in the presence of alkylene glycols which are also normally present in antifreezes. Thus, it has been previously proposed to use a stabilizer to prevent the gelation of the alkali metal silicate in the antifreeze composition.

Several types of silicon compounds have hitherto been described as suitable stabilizers. For instance, US Patents 3234144 and 4241012 describe the use of amino-siloxanes as stabilizers; US Patents 3312622 and 4241011 discloses carboxy siloxanes as suitable stabilizers; and US 3337496 and US 4210548 recommend the use of hydroxyalkyl derivatives of siloxanes.

One of the major problems with the previously described stabilizers is that they do not have adequate solubility in the alkylene glycol and/or water which form the basis of the antifreeze composition.

Moreover, the low solubility of conventional stabilizers makes it particularly difficult to produce the corrosive inhibitors in concentrated form. Such concentrates, containing large amounts of inhibitors in alkylene glycol (e.g. near the solubility limits), are

generally not stable from gelation over storage period of several months. Thus, it would be highly desirable to develop stabilizers which would allow the production of inhibitor concentrates which could be stored for long periods and then blended as desired into antifreeze compositions.

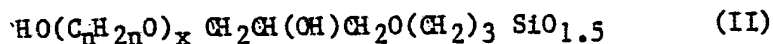
It has now been found that the solubility problems encountered with prior art stabilisers can be mitigated by using polyoxyalkylene derivatives of siloxanes. Moreover, by incorporating a polyalkylene oxide into the siloxane molecule, the stabilisers have improved effectiveness for retarding gelation in concentrated inhibitor compositions.

Accordingly, the present invention provides a stabiliser for silicate corrosion inhibitors useful in polyalkylene glycol compositions comprising an organosiloxane containing a polyoxyalkylene end chain of the general formula:



wherein  $x$  is a number from 5 to 10 and  
 $n$  is a number from 2 to 4.

Also provided in a separate embodiment is a organosiloxane compound of the general formula:



wherein  $x$  and  $n$  are as defined in formula I.

In still another embodiment, the present invention provides an antifreeze composition comprising an alkylene glycol, a silicate corrosion inhibitor and the stabiliser of formula II.

The polyoxyalkylene end chain is as illustrated in formula I where  $n$  is a number from 2 to 4, preferably 2 and  $x$  is a number from 5 to 10, preferably 6 to 9 when  $n$  is 2. Most preferred are stabilisers of formula I wherein  $n$  is 2 and  $x$  is from 6 to 9.

The stabiliser of this invention is generally prepared by reaction of appropriate polyalkylene glycol with a gamma glycidyl oxyalkyl trialkoxysilane at elevated temperatures and atmospheric pressures.

In a preferred technique, the stabiliser is prepared by reacting glycidyl oxypropyl trimethoxysilane (GOTS) with a molar

excess of the appropriate polyoxyalkylene glycol, for example 1 mole of GOTS with 5.3 moles of polyethylene glycol (in excess of stoichiometric amount to avoid polymer formation). The reaction is suitably carried out in a liquid medium and in an inert atmosphere.

5 The reaction is conducted at a temperature from 80°C to 200°, preferably from 100°C to 150°C and at atmospheric pressure in the presence of a hydroxide catalyst (preferably sodium or potassium hydroxide). The polyoxyalkylene derivative of GOTS so formed can be used as such, without any further treatment. GOTS is commercially

10 available from Dynamit Nobel and Union Carbide.

The amount of the inventive stabiliser used in an antifreeze composition will depend upon the anti-corrosive formulation and in particular the amount of corrosion inhibitor but is suitably in the range from 0.05% to 3% by weight based on the total antifreeze

15 composition.

Preferably, the alkylene glycol is propylene glycol, ethylene glycol or a mixture thereof.

The siloxanes of this invention and the effectiveness of the compositions produced therefrom are illustrated with reference to

20 the following Example and Comparative Tests.

However, the Examples should not be construed as limiting the scope of this invention which includes equivalent embodiments, modifications and variations falling within the scope of the attached claims.

#### 25 Examples and Comparative Tests

An antifreeze concentrate was prepared by dissolving the following inhibitors (w/w%) in ethylene glycol.

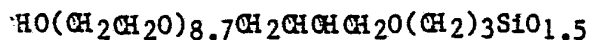
	Borax	5.3
	Sodium hydroxide	0.5
30	Sodium benzoate	10.0
	Tolyltriazole	0.3
	Aqueous solution of potassium trisilicate (5.332% w/w)	10.0

The concentrate so formed was divided into 100g aliquots.

#### Example

35 To a 100g aliquot of the concentrate was added 0.00144 moles of

a commercially available modified siloxane of the formula:



The thus prepared mixture was subjected to an accelerated storage test by storing at 66°C storage for 1 day at this  
5 temperature being approximately equivalent to storage for 1 month at 25°C.

The mixture remained a bright and clear liquid after 6 days with no gelation showing that the silicate had been stabilized.

#### Comparative Test 1

10 A 100g control portion of the concentrate with no stabilizer was stored under the same conditions as in the Example above. This formulation gelled after storage for 1 day, showing the silicate to be relatively unstable.

#### Comparative Test 2

15 To a 100g portion of the concentrate was added 0.00144 moles of a modified siloxane of the formula  $\text{CH}_2\text{OHCH}(\text{CH}_3)\text{CH}_2\text{O}(\text{CH}_2)_3\text{SiO}_{1.5}$ . This formulation was also stored under the same conditions as the Example above and the formulation gelled after 2 days.

## Claims:

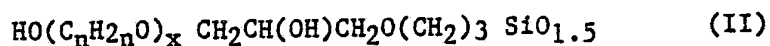
1. A stabiliser for silicate corrosion inhibitors useful in polyalkylene glycol compositions comprising an organosiloxane containing a polyoxyalkylene end chain of the general formula:



5 wherein  $x$  is a number from 5 to 10 and  
 $n$  is a number from 2 to 4.

2. The stabiliser of claim 1 wherein  $n$  is 2 and  $x$  is from 6 to 9.

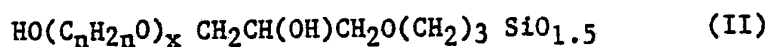
3. An organosiloxane compound of the general formula



10 wherein  $x$  is a number from 5 to 10 and  
 $n$  is a number from 2 to 4.

4. The organosiloxane compound of claim 3 wherein  $x$  is 6 to 9 and  $n$  is 2.

5. An antifreeze composition comprising an alkylene glycol, a  
15 silicate inhibitor and a stabiliser of the general formula:

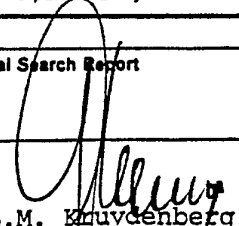


6. The antifreeze composition of claim 5 wherein in the stabiliser of formula (II)  $n$  is 6 to 9 and  $n$  is 2.

7. The antifreeze composition of claim 5 wherein the alkylene  
20 glycol is propylene glycol, ethylene glycol or mixtures thereof.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 85/00060

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC <sup>4</sup> : C 09 K 5/00		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
IPC <sup>4</sup>	C 09 K; C 23 F; C 08 L	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup></b>		
Category <sup>9</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
A	US, A, 4287077 (PHILLIP) 1 September 1981 see claims 1,2 ---	1-7
A	EP, A, 0097583 (UNION CARBIDE) 4 January 1984 see claims 1,8 ---	1-7
A	US, A, 3337496 (PINES) 22 August 1967 see column 1, lines 9-14; claim 1 ---	1-7
A	US, A, 2846458 (HALUSKA) 5 August 1958 see column 1, lines 29-36; claim 1 ---	1-7
A	US, A, 4010110 (COSENTINO) 1 March 1977 see column 1, lines 17-23; claim 1 ---	1-7
A	US, A, 3398174 (BARNES) 20 August 1968 ---	
A	DE, A, 2054506 (GRACE) 13 May 1971 -----	
<p><sup>10</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"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</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"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.</p> <p>"&amp;" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
28th May 1985	20 JUN 1985	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	 G.L.M. Kruidenberg	



ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/GB 8500060 (SA 8784)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 14/06/85

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4287077	01/09/81	EP-A, B 0029728	03/06/81
		AU-A- 6464380	28/05/81
		CA-A- 1145923	10/05/83
		AU-B- 535653	29/03/84
EP-A- 0097583	04/01/84	US-A- 4404114	13/09/83
		JP-A- 59006266	13/01/84
US-A- 3337496		US-A- 3341469	
		FR-A- 1324490	
US-A- 2846458		None	
US-A- 4010110	01/03/77	US-A- 3962119	08/06/76
US-A- 3398174		NL-A- 6601308	04/08/66
		GB-A- 1107192	
		FR-A- 1462752	
		DE-A- 1267220	
		NL-C- 125456	
DE-A- 2054506	13/05/71	FR-A- 2071843	17/09/71
		US-A- 3666404	30/05/72
		GB-A- 1301306	29/12/72
		CA-A- 939135	01/01/74
		CA-A- 939136	01/01/74

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