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(54) Glycol compositions containing an ether modified silicone.

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Description

The present invention provides a gelation resistant aqueous glycol or glycol ether composition.

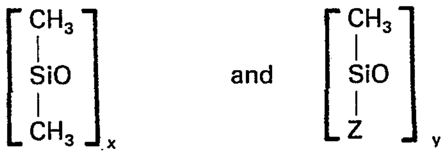
Antifreeze compositions containing glycols and various corrosion inhibitors are well known in the prior art as is illustrated by U.S. patents 3,282,846, and 3,362,910. The use of the relatively inexpensive and effective borax and silicates in glycol formulations is well illustrated by these patents. It is conventional in this art to make a glycol concentrate which is then sold to end users for use as a coolant in automotive radiators after dilution with water.

In the past, it has been found that glycol concentrates prepared using conventional corrosion inhibitors such as borax and silicates had a tendency to develop irreversible silicate gels upon standing for a period of time in a warehouse or store. The end user, when he attempted to pour the glycol concentrate into his automotive radiator found that the concentrate had developed "slugs" or gels which either did not pour readily or which tumbled out in discrete masses along with the liquid. The present invention was developed to eliminate this gel formation.

In U.S. patent 3,312,622 there is disclosed a corrosion resistant glycol composition containing an organo-silicon copolymer having carboxylate salt groups and silicate groups.

In U.S. patent 4,149,985 there is disclosed that a gelation resistant glycol composition containing borate and silicate additives can be made wherein the order of addition of the additives and the pH of the solution is closely controlled in order to obtain the gelation resistant formulation.

It has now been discovered that the shelf life or gelation resistance of single phase aqueous glycol or glycol ether compositions can be improved by the addition to the glycol compositions of 0.001 to 1.0 percent of a glycol soluble ether modified silicone having the repeating units



$$\left[\begin{array}{c}CH_3\\ |\\ SiO\\ |\\ CH_3\end{array}\right]_x \quad \text{and} \quad \left[\begin{array}{c}CH_3\\ |\\ SiO\\ |\\ Z\end{array}\right]_y$$

wherein

x has an average value range from 1.8 to 6.8

Y has an average value range from 1 to 4

Z has the formula

$$—R\!\left(C_nH_{2n}O\right)_m R_1$$

where

n is 2 or 3

m has an average value such that the average molecular weight of the polyoxyalkylene chain is in the range 100—400

R is an alkylene chain of 2—4 carbons and

R_1 is hydrogen or an alkyl group of 1—4 carbons.

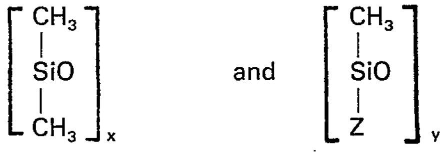
This anti-gelation additive is relatively cheap and effective in the presence of the other well-known corrosion inhibitors generally present in such compositions such as alkali metal silicates, borates, tolyltriazoles, mercaptobenzotriazoles, nitrates, nitrites, phosphates and benzoates.

The present invention is an aqueous composition comprising

(A) 85 to 98 percent by weight of the total composition of an alkylene glycol, an alkylene glycol ether, or mixtures thereof,

(B) 0.025 to 1.0 percent by weight of the total composition of an alkali metal silicate,

(C) 0.001 to 1.0 percent by weight of the total composition of a glycol soluble ether modified silicone copolymer comprising the repeating units



$$\left[\begin{array}{c}CH_3\\ |\\ SiO\\ |\\ CH_3\end{array}\right]_x \quad \text{and} \quad \left[\begin{array}{c}CH_3\\ |\\ SiO\\ |\\ Z\end{array}\right]_y$$

wherein

x has an average value range from 1.8 to 6.8

Y has an average value range from 1 to 4

Z has the formula

$$—R\!\left(C_nH_{2n}O\right)_m R_1$$

where

n is 2 or 3

m has an average value such that the average molecular weight of the polyoxyalkylene chain is in the range 100—400

R is an alkylene chain of 2—4 carbons

R_1 is hydrogen or an alkyl group of 1—4 carbons, and

(D) any remainder being water and one or more other corrosion inhibitors.

The glycols and glycol ethers which can be used in the present composition are (1) glycols such as ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, (2) glycol monoethers such as the methyl, ethyl propyl and butyl ether of ethylene glycol, diethylene glycol, propylene glycol and dipropylene glycol, and (3) glycol diethers such as the methyl and ethyl diethers of ethylene glycol, diethylene glycol, and dipropylene glycol.

Ethylene glycol and the monomethyl ether of propylene glycol, i.e., methoxy propanol are particularly preferred.

The following are examples of known corrosion inhibitors and additives which can be used in the present invention.

Alkali metal silicates such as sodium metasilicate, potassium metasilicate or lithium metasilicate.

Alkali metal borates such as sodium tetraborate, potassium tetraborate, sodium metaborate, and potassium metaborate.

Alkali metal mercaptobenzotriazoles, and alkali metal tolyltriazoles.

Alkali metal nitrates such as sodium nitrate and potassium nitrate, and alkali metal nitrites such as potassium and sodium nitrite.

Alkali metal phosphates such as sodium phosphate and potassium phosphate, alkali metal benzoates, and various antifoams and dyes if desired.

In the process of making the compositions of this invention, one or more of the above glycols are mixed with one of the above non-silicate corrosion inhibitors and sufficient amounts of other inhibitors such as mercaptobenzothiazoles, tolyltriazoles, nitrates, and phosphate inhibitors necessary for corrosion protection. An effective amount of the above siloxane is added next. The pH of the solution is then adjusted to the desired pH range of 7—12, and preferably 9—11.0, by adding a basic inorganic compound in aqueous solution such as an alkali metal hydroxide, carbonate, or phosphate. One of the above alkali metal silicates is then added to produce a corrosion and gelation resistant glycol composition.

For the purposes of this invention, an amount of the siloxane which will give a gelation resistant glycol composition is an amount ranging from 0.001 to 1.0 percent by weight and preferably in the range from 0.01 to 0.025 percent by weight based on the total weight of the composition.

The use of the above corrosion inhibitors when used in a corrosion inhibiting amount is well known in the prior art. Of course, this amount will vary for each inhibitor but the amounts used of the silicates and borates are:

0.025 to 1.0 percent by weight based on the total solution weight of silicates and 0.1 to 2.0 percent by weight of borates. Preferably, these ranges are 0.05 to 0.50 percent for the silicates and 0.5 to 1.5 percent for the borates.

In this invention, it has been found that when the borate levels are at the higher end of the desired range (0.5 to 2.0 percent by weight), the amount of silicate that can be added must be in the lower end of the desired range of silicate level (0.025 to 0.3 percent by weight). It is not possible to set forth exactly the amount of silicate to be used in each instance due to the complicating influence of the other corrosion inhibitors such as the aforementioned triazoles, nitrates, nitrites, and phosphates. However, one can by a simple accelerated aging test determine the amount of silicate which when added will give the desired gelation resistance.

An accelerated aging test was used in the examples and controls that follow to estimate the shelf life of the compositions. It was performed by placing a sample of the glycol composition in an oven controlled at 150°F (66°C) and measuring the number of hours or days before the composition begins to gel. By comparing the room temperature (25°C) aging of the same samples, it has been found that one day at 150°F (66°C) is approximately equal to one month at room temperature (77°F or 25°C).

The siloxane compounds used herein can be prepared by reacting a poly(dimethyl)siloxane having an average molecular weight of 200 to 500 and an average of two or more silicon bonded hydrogen atoms with an alkylene capped glycol or glycol or ether having the formula

$$CH_2{=}CH\left(CH_2\right)_p{-}O\left(C_nH_{2n}O\right)_mR_1$$

where

p is 1 or 2

n is 2 or 3

m has an average value such that the average molecular weight of the polyoxyalkylene chain is in the range 100—400

R_1 is hydrogen or alkyl groups of 1—4 carbons.

The reaction is well known from U.S. patents 3,179,622 and 2,846,458 and British patent 955,916. The reaction is illustrated by the preparations 1—4 hereinafter set forth.

The invention is further illustrated but not limited by the following examples and controls:

Control 1

Sodium metaborate $Na_2B_4O_7''5H_2O$ (13.0 g) was added to 960 g of ethylene glycol and stirred until dissolution was complete. A 33 1/3% aqueous $NaNO_3$ solution (6.0 g) was added and stirred until well dispersed, followed by 2 gms of a 50% aqueous solution of sodium tolyltriazole. The pH of the solution was then adjusted with aqueous caustic to 8.45 and 10 gms of a 10% aqueous solution of sodium metasilicate pentahydrate ($Na_2SiO_3''5H_2O$) was added with stirring during a 2 minute addition time. The final pH of the antifreeze solution was 10.0 and it contained 1.3% sodium metaborate pentahydrate and 0.1% sodium metasilicate pentahydrate. The solution prepared in this manner was found to have a shelf life as determined by the above accelerated aging test of about 7—10 days which is equivalent to about 7—10 months at room temperature (24°C).

Example 1

The procedure described in control 1 was repeated except that just before the pH of the solution was adjusted to 8.45, 100 parts per million of dimethyl siloxane modified with the allyl methyl ether of dipropylene glycol was added. The modified silicone was made by preparation 1 hereinafter.

The solution was found to have a shelf life of 180 days by the above aging test which is equivalent to about 180 months at room temperature.

In order to compare the corrosion properties of the above formulations, the following tests were run and reported in Table I.

The corrosion test data was obtained by the use of ASTM D1384—70, Corrosion Test for Engine Coolants in Glassware. In this method, specimens of metals typical of those present in automotive cooling systems are totally immersed in the test antifreeze solution with aeration for 336 hours at 190°F (88°C). The corrosion inhibitive properties are evaluated on the basis of the weight changes incurred by the specimens. Each test is run in duplicate and the average weight change is determined for each metal. Acceptable minimum weight losses are those less than 20 milligrams.

TABLE I

Sample	Test metal	Duplicate weight loss (mg)	Avg. weight loss (mg)
Control 1	copper	3.5, 3.7	4
	solder	3.0, 4.5	4
	brass	3.2, 4.5	4
	steel	0.7, 0.6	1
	cast iron	3.6, 3.3	3
	aluminum	3.5, +1.2	1
Example 1	copper	1.9, 1.8	2
	solder	12.7, 13.0	13
	brass	1.8, 1.7	2
	steel	0.6, 1.0	1
	cast iron	1.3, 0.1	1
	aluminum	+6.9, +1.9	+4

Substantially, the same results were obtained when the modified siloxane was added with the sodium silicate solution.

From the above data is seen that while the corrosion properties of the control and Example 1 are about the same, the shelf life of Example 1 is at least about 18 times longer than the control.

Control 2

The procedure of Control 1 was repeated except that the pH was first adjusted to 9.5, then 20 grams of a 10% aqueous solution of sodium metasilicate pentahydrate was added to give a 0.2% solution of the silicate, and the final pH was adjusted to 11.0.

Because of the higher silicate level, this formulation was found to have an estimated shelf life of 14 months.

Example 2

The procedure of Control 2 was repeated with the addition of 100 ppm of the modified silicone used in Example 1 to give a solution containing 0.2% sodium silicate and 0.01% of the siloxane. The estimated shelf life of this formulation was 90 months.

Table II shows the corrosion test data obtained for Controls 1, 2, and Example 2 by the use of ASTM D2570—73, Standard Method for Simulated Service Corrosion Testing of Engine Coolants. In this method, an engine coolant is circulated for 1064 hours at 190°F (88°C) at 30 to 35 gal./min. (135—160 l/min) in a flow loop consisting of a metal reservoir, an automotive coolant pump, an automotive radiator, and connecting rubber hoses. Test specimens representative of engine cooling system metals are mounted inside the reservoir, which simulates an engine cylinder block. At the end of the test period, the corrosion inhibiting properties of the coolant are determined by measuring the weight losses of the test specimens and by visual examination of the interior surfaces of the components.

TABLE II

Sample	Metal	Average weight loss (mg)
Control 1*	copper	2
	solder**	68
	brass	1
	steel	+2
	cast iron	+2
	aluminum**	65
Control 2	copper	2
	solder**	18
	brass	3
	steel	11
	cast iron	2
	aluminum**	+3
Example 2	copper	3
	solder**	47
	brass	5
	steel	1
	cast iron	1
	aluminum**	15

Acceptable minimum weight loss is less than 20 mg (except for solder and aluminum).

* Average of two test runs.

** Acceptable minimum weight loss is less than 60 mg.

The corrosion test data of Table II shows the improvement in corrosion inhibiting properties when the amount of $Na_2SiO_3''5H_2O$ in Control 1 is increased to 0.2%. However, in order to prevent gelation on aging at the 0.2% silicate level the ether modified siloxane must be used as a stabilizer as shown in Example 2.

Preparation 1

Into a 500 ml flask was added 50 gms of the allyl monoether of dipropylene glycol, 51.1 gms of a polydimethyl siloxane having an average of two hydrogen siloxane groups and having a molecular weight of 356, 125 gms of toluene and 1.1 gms of a 2 percent solution of H_2PtCl_2"$6H_2O$ in isopropanol. The mixture was stirred and heated under reflux slowly. At 60—65°C an exotherm took place which raised the temperature to 110°C. The solution was heated at 106—108°C for 2.5 hours under reflux conditions. The product was recovered by vacuum stripping at 60°C. The product was identified as a dimethylsiloxane modified by the allyl ether of dipropylene glycol.

Preparation 2

The procedure of preparation 1 was repeated using 60 gms of the allyl monoether of tripropylene glycol, 46 gms of the above siloxane, and 1.1 gms of the chloroplatinic acid solution. The product was identified as a dimethyl siloxane modified by the allyl ether of tripropylene glycol.

Preparation 3

The procedure of preparation 1 was repeated using 65 gms of the allyl monoether of tetrapropylene glycol, 39.9 gms of the above siloxane, and 1.1 gms of the chloroplatinic acid solution. The product was identified as a dimethyl siloxane modified by the allyl ether of tetrapropylene glycol.

Preparation 4

The procedure of preparation 1 was repeated using 75 gms of the allyl monoether of decaethylene glycol, 26.7 gms of the above siloxane, and 1.1 gms of the chloroplatinic acid. The product was identified as a dimethyl siloxane modified by the allyl ether of decaethylene glycol.

Example 3

The procedure of Example 2 was repeated in triplicate using 100 ppm of the dimethyl siloxane modified by the monoallyl ether of dipropylene glycol (preparation 1).

The three solutions were found to have an estimated shelf life at room temperature of 30 months maximum and 25 months minimum.

Example 4

The procedure of Example 2 was repeated in triplicate with 100 ppm of the dimethyl siloxane modified by the monoallyl ether of tripropylene glycol (preparation 2). The estimated shelf life was found to be 20 months maximum and 15 months minimum.

Example 5

The procedure of Example 2 was repeated in triplicate using 100 ppm of the dimethyl siloxane modified by the monoallyl ether of tetrapropylene glycol (preparation 3). The estimated shelf life was found to be 20 months maximum and 15 months minimum.

Example 6

The procedure of Example 2 was repeated in triplicate using 100 ppm of the dimethyl siloxane modified by the monoallyl ether of decaethylene glycol (preparation 4). The estimated shelf life was found to be 20 months maximum and 15 months minimum.

Claims

1. A gellation resistant aqueous glycol composition comprising:

(A) 85 to 98 percent by weight of the total composition of an alkylene glycol, an alkylene glycol, an alkylene glycol ether, or mixtures thereof

(B) 0.025 to 1.0 percent by weight of the total composition of an alkali metal silicate,

(C) 0.001 to 1.0 percent by weight of the total composition of a glycol soluble ether modified silicone copolymer comprising the repeating units

$$\left[\begin{matrix} CH_3 \\ | \\ SiO \\ | \\ CH_3 \end{matrix}\right]_x \quad \text{and} \quad \left[\begin{matrix} CH_3 \\ | \\ SiO \\ | \\ Z \end{matrix}\right]_y$$

wherein

x has an average value in the range of from 1.8 to 6.8

y has an average value in the range of from 1 to 4

Z has the formula

$$-R\left(C_nH_{2n}O\right)_mR_1$$

where

n is 2 or 3

m has an average value such that the average molecular weight of the polyoxyalkylene chain is in the range of from 100—400

R is an alkylene chain containing from 2 to 4 carbon atoms and

R_1 is a hydrogen atom or an alkyl group containing 1 to 4 carbon atoms, and

(D) any remainder being water and one or more other corrosion inhibitors.

2. A gellation resistant aqueous glycol as claimed in Claim 1 comprising:

(A) 85 to 98 percent by weight of the total composition of an alkylene glycol,

(B) 0.1 to 2.0 percent by weight of the total composition of an alkali metal borate,

(C) 0.025 to 1.0 percent by weight of the total composition of an alkali metal silicate,

(D) 0.001 to 1.0 percent by weight of the total composition of a glycol soluble ether modified silicone polymer copolymer comprising the repeating units

$$\left[\begin{array}{c}CH_3\\ |\\ SiO\\ |\\ CH_3\end{array}\right]_x \qquad \left[\begin{array}{c}CH_3\\ |\\ SiO\\ |\\ Z\end{array}\right]_y$$

wherein

x, y, Z, R and R_1 are as defined in Claim 1, and

(E) any remainder being water.

3. A composition as claimed in Claim 1 or Claim 2 wherein the alkylene glycol is ethylene glycol.

4. A composition as claimed in Claim 1 or Claim 2 wherein the alkylene glycol ether is the monomethyl ether of propylene glycol.

5. A composition as claimed in Claim 1 or Claim 2 the amount of silicone copolymer is in the range of from 0.01 to 0.025 percent by weight.

Patentansprüche

1. Eine gelatinierungsfeste wässrige Glykolzusammensetzung, enthaltend:

(A) 85 bis 98 Gewichtsprozent, bezogen auf das Gesamtgewicht der Zusammensetzung, eines Alkylenglykols, eines Alkylenglykoläthers oder eines Gemisches aus denselben,

(B) 0.025 bis 1.0 Gewichtsprozent, bezogen auf das Gesamtgewicht der Zusammensetzung, eines Alkalimetallsilikats,

(C) 0.001 bis 1.0 Gewichtsprozent, bezogen auf das Gesamtgewicht der Zusammensetzung, eines glykollöslichen äthermodifizierten Silikoncopolymers mit den folgenden sich wiederholenden Einheiten:

$$\left[\begin{array}{c}CH_3\\ |\\ SiO\\ |\\ CH_3\end{array}\right]_x \quad \text{und} \quad \left[\begin{array}{c}CH_3\\ |\\ SiO\\ |\\ Z\end{array}\right]_y$$

in denen

x einen Mittelwert zwischen 1,8 und 6,8 bedeutet,

y einen Mittelwert zwischen 1 und 4 bedeutet,

Z die Formel

$$-R\left(C_nH_{2n}O\right)_mR_1$$

ist,

in der n 2 oder 3 ist,

m einen solchen Mittelwert hat, dass das durchschnittliche Molekularmittelgewicht der Polyoxyalkylen-Kette zwischen 100 und 400 liegt, R eine Alkylen-Kette mit 2 bis 4 Kohlenstoffatomen ist, und

R_1 ein Wasserstoffatom oder eine Alkylgruppe mit 1 bis 4 Kohlenstoffatomen ist, und

(D) wobei etwaiger Rest Wasser und ein oder mehrere sonstige Korrosionshemmer ist.

2. Ein gelatinierungsfeste wässrige Glykolzusammensetzung gemäss Anspruch 1, enthaltend:

(A) 85 bis 98 Gewichtsprozent, bezogen auf das Gesamtgewicht der Zusammensetzung, eines Alkylenglykols

(B) 0.1 bis 2.0 Gewichtsprozent, bezogen auf das Gesamtgewicht der Zusammensetzung, eines Alkalimetallborats,

(C) 0.025 bis 1.0 Gewichtsprozent, bezogen auf das Gesamtgewicht der Zusammensetzung, eines Alkalimetallsilikats,

(D) 0.001 bis 1.0 Gewichtsprozent, bezogen auf das Gesamtgewicht der Zusammensetzung, eines glykollöslichen äthermodifizierten Silikoncopolymers mit den sich wiederholenden Einheiten:

$$\left[\begin{array}{c}CH_3\\|\\SiO\\|\\CH_3\end{array}\right]_x \qquad \left[\begin{array}{c}CH_3\\|\\SiO\\|\\Z\end{array}\right]_y$$

in denen

x, y, Z, R und R_1 sind wie im Anspruch 1 definiert, und

(E) wobei etwaiger Rest Wasser ist

3. Eine Zusammensetzung gemäss Anspruch 1 oder 2, in der der Alkylenglykol Äthylenglykol ist.

4. Eine Zusammensetzung gemäss Anspruch 1 oder 2, in der der Alkylenglykoläther Propylenglykolmonomethyläther ist.

5. Eine Zusammensetzung gemäss Anspruch 1 oder 2, in der die Menge des Silikoncopolymers zwischen 0.01 und 0.025 Gewichtsprozent beträgt.

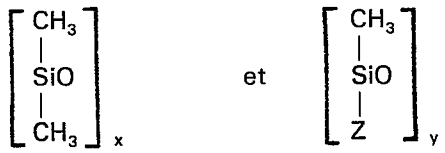
Revendications

1. Composition aqueuse de glycol résistant à la gélification, comprenant:

(A) 85 à 98% en poids, par rapport au poids de la composition totale, d'un alkylène-glycol, d'un éther d'alkylène-glycol ou de mélanges de ceux-ci,

(B) 0,025 à 1,0% en poids, par rapport au poids de la composition totale, d'un silicate de métal alcalin,

(C) 0,001 à 1,0% en poids, par rapport au poids de la composition totale, d'un copolymère de silicone modifié par un éther soluble de glycol comprenant les motifs de récurrence



$$\left[\begin{array}{c}CH_3\\|\\SiO\\|\\CH_3\end{array}\right]_x \quad \text{et} \quad \left[\begin{array}{c}CH_3\\|\\SiO\\|\\Z\end{array}\right]_y$$

dans lesquels

x a une valeur moyenne de 1,8 à 6,8

y a une valeur moyenne de 1 à 4

Z répond à la formule:

$$-R(C_nH_{2n}O)_mR_1$$

dans laquelle

n est 2 ou 3

m a une valeur moyenne telle, que le poids moléculaire moyen de la chaîne polyoxyalkylène soit compris entre 100 et 400

R est une chaîne alkylène de 2 à 4 atomes de carbone, et

R_1 est un atome d'hydrogène ou un radical alkyle de 1 à 4 atomes de carbone; et

(D) tout complément étant l'eau et un ou plusieurs autres inhibiteurs de corrosion.

2. Glycol aqueux résistant à la gélification selon la revendication 1, comprenant:

(A) 85 à 98% en poids, par rapport au poids de la composition totale, d'un alkylène-glycol;

(B) 0,1 à 2,0% en poids, par rapport au poids de la composition totale, d'un borate de métal alcalin;

(C) 0,025 à 1,0% en poids, par rapport au poids de la composition totale, d'un silicate de métal alcalin;

(D) 0,001 à 1,0% en poids, par rapport au poids de la composition totale, d'un copolymère de silicone modifié par un éther soluble de glycol, comprenant les motifs de récurrence:

$$\left[\begin{array}{c}CH_3\\ |\\ SiO\\ |\\ CH_3\end{array}\right]_x \qquad \left[\begin{array}{c}CH_3\\ |\\ SiO\\ |\\ Z\end{array}\right]_y$$

dans lesquels

x, y, Z, R et R_1 sont tels que définis dans la revendication 1 ; et

(E) tout complément éventuel étant de l'eau.

3. Composition selon la revendication 1 ou 2, dans laquelle l'alkylène-glycol est l'éthylène-glycol.

4. Composition selon la revendication 1 ou 2, dans laquelle l'éther d'alkylène-glycol est l'éther monométhylique du propylène-glycol.

5. Composition selon la revendication 1 ou 2, dans laquelle la quantité de copolymère de silicone est comprise entre 0,01 et 0,025% en poids.