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(54) Title: CORROSION INHIBITOR

(57) Abstract: It has surprisingly been discovered that simple diols and triols work as corrosion inhibitors in concentrated organic and inorganic acids, e.g. used as additives in metallic equipment in factories and plants. These corrosion inhibitors are cheap and readily available in large quantities. The diol and triol also reduces evaporation of the acid, and thus improves the working environment.

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CORROSION INHIBITOR

The present invention concerns the discovery that a diol or triol or as mixture thereof provides a corrosion-reducing or inhibiting effect when added to acids or acid containing compositions used in metal or metallic equipment in production factories or plants for reducing or inhibiting microbial growth. Such factories or plants may be factories or plants for silage of grass, ensilage of fish and/or fish products, continued treatment/ensilage of slaughterhouse waste and food waste or in drinking facilities for farm house animals such as poultry or pigs. Tanneries, metallurgic industry and pulp mills are other examples of factories or plants where large amounts of acids are used.

Organic acids have many beneficial effects when it comes to controlling microbial growth. They are thus frequently used for the preservation of organic materials. Propionic acid is used as a grain preservative, for silage of grass and as a feed additive. Formic acid is used in ensilage of fish, slaughterhouse waste, food waste and grass, and also in pig and chicken feed. Acetic acid is used for conservation of fish. Benzoic acid is used for fish ensilage. Other acids, or mixture of acids, are also used. Organic acids are also used in the drinking water for pigs and poultry, among others. The addition of organic acids to compound feed for pigs, sheep, goats, poultry, cattle, horses, dogs, cats and fur-bearing animals has an efficacious effect on their growth and health. Further, the acid addition to compound feed reduces the amount of consumed compound feed per kg of growth without the increased growth affecting the quality of the meat. This reduces feed cost by reducing the feeding period and promoting better housing utilization.

Strong acids like sulfuric acid, sulfurous acid and hydrochloric acids are used in many processes. Tanning, metallurgy and pulping are just a few examples.

There are a number of problems, however, with using acids, and in particular strong acids such as formic acid or mineral acids, including the corrosion of the equipment. Acids are corrosive and yearly corrosion from handling these acids costs millions of dollar. There is considerable corrosion on storage tanks, pipes, valves and the mixing equipment in the production line for pelleted feed in particular. This drives up the operating costs and leads to the added burden of increased maintenance and system monitoring.

There are also problems with using volatile for those handling the product. Formic acid is particularly corrosive to skin and can cause damage from etching, which is why it full body protection is needed. As an example during pelleting process the temperature rises to 80-95 °C, and some of the acid will evaporate. This leads to evaporation of some of the acid, the vapours of which can be dangerous on inhalation. Loss of acid through evaporation will not only cause environmental problems, but also have an economic cost.

Previously some of the adverse effects have been relieved by adding a polymeric strong acid such as lignosulfonic acid or its salt (Patent WO 00/27220, PCT/NO99/00309).

In the present invention the above-mentioned problems associated with the use of acids have been reduced by adding a diol or triol, in particular glycerol. Surprisingly, it has been shown that the reduced corrosion rates goes far beyond that expected from a dilution of the acid.

By diol is meant any organic compound with at two hydroxyl group, e.g. ethylene glycol or propylene glycol. By triol is meant any organic compound with three hydroxyl groups, e.g. glycerol. Diols and triols can be produced by fermentation, by hydrolysis or by trans-esterification. Glycerol is produced in large quantities from the saponification of fats and the trans-esterification of fats to fatty acid methyl esters during biodiesel production.

The diol or triol is added in quantities from 10 to 90% of the final mixture with the acids, preferably from 40 to 60%.

Sugar and sugar alcohols have previously been described as corrosion inhibitors (FR 2 391 261A). The advantages of simple diols and triols are several. They are cheaper. They are liquid at room temperature, and thus easier to use in any formulation. With the use of a diol like glycol or the triol glycerol we are not using scarce food resources as chemical raw materials.

Glycerol has been shown to reduce skin corrosion in a formic acid that has been partly neutralised with ammonia (NO 307 591 B). We here show that diols or triols also function as a corrosion inhibitor for metals without any neutralisation of the acids.

The following examples are meant to illustrate the invention without limiting its scope in any way.

EXAMPLES

Corrosion tests

Carbon steel coupons C1018 were used for the corrosion tests. The coupons were sonicated in acetone for 10 minutes, then dried in a heating cabinet, cooled in a desiccator and weighed. They were hung in polypropylene strips inside the test bottles filled with acid and the added corrosion inhibitor. The bottles were sealed with plastic film to prevent evaporation of the acid. The test bottles were placed on magnetic stirrers to prevent diffusion gradients within the solution. After 3 days the steel coupons were removed form the bottles and washed with warm water and acetone before they were dried in a heating cabinet, cooled in a desiccator and weighed. All experiments were done in duplicate and the average corrosion rates are given.

Corrosion rates, CR (mm/year), were determined from the weight loss of the steel coupons using this equation:

$$CR = \frac{\text{Weight loss (g)} * 365\ \text{d/year} * 10\ \text{mm/cm}}{\rho\ \text{Steel (g/cm}^3) * \text{Surface area(cm}^2) * \text{d}}$$

ρSteel = 7,718 g/cm^3

Surface area = 27, 2 cm^2

The results from the different tests are shown in the tables below.

Table 1. The effect of glycerol concentration for a strong organic acid.

Composition	Corrosion rate / mm/year	Improvement / %
10% water – 90% formic acid	6.7	---
10% glycerol – 90% formic acid	4.1	38.8
25% water – 75% formic acid	5.0	---
25% glycerol – 75% formic acid	3.2	36.0
50% water – 50% formic acid	7.5	---
50% lignosulfonate solution – 50% formic acid	2.8	62.7
50% glycerol – 50% formic acid	1.3	82.7

We see that at all concentrations glycerol is at least as effective as the commercially used lignosulfonates.

Table 2. The effect of glycerol concentration for a weak organic acid.

Composition	Corrosion rate / mm/year	Improvement / %
10% water – 90% propionic acid	4.52	---
10% glycerol – 90% propionic acid	0.70	84.5
25% water – 75% propionic acid	5.57	---
25% lignosulfonate solution – 75% propionic acid	0.55	90.1
25% glycerol – 75% propionic acid	0.06	99.0
50% water – 50% propionic acid	2.80	---
50% lignosulfonate solution – 50% propionic acid	1.15	58.9
50% glycerol – 50% propionic acid	0.031	98.9

We see that at all concentrations glycerol is at least as effective as the commerically used lignosulfonates.

Table 3. The effect for various acids in a 50:50 wt% mixing ratio.

Composition	Corrosion rate / mm/year	Improvement / %
50% water – 50% concentrated hydrochloric acid	114.8	---
50% glycerol – 50% concentrated hydrochloric acid	83.8	27.0
50% water – 50% sulfuric acid (30%)	181	---
50% glycerol – 50% sulfuric acid (30%)	25.9	85.7
50% water – 50% propionic acid	2.8	---
50% glycerol – 50% propionic acid	1.2	58.9
50% water – 50% formic acid	7.5	---
50% glycerol – 50% formic acid	1.3	82.7

We see that glycerol is effective for several mineral acids and organic acids.

Table 4. The effect of various alcohols.

Composition	Corrosion rate / mm/year	Improvement / %
50% water – 50% formic acid	7.5	---
50% glycerol – 50% formic acid	1.3	82.7
50% glycol – 50% formic acid	2.9	61.7
50% ethanol – 50% formic acid	9.8	-31.1

We see that the diol and triol shows good corrosion inhibition, while the simple alcohol does not.

Evaporation tests

500 ml of 50:50 wt% glycerol:formic acid, lignosulfonate:formic acid, water:formic acid solutions were made. Pure formic acid was included as a reference. Exactly 100 g of each solution was placed in 2 different beakers.

The samples were kept at room temperature with and without stirring. The weight was recorded at 4 hours, 26 hours, 58 hours and 89 hours. The results are presented in figure 1 and 2. We see that all additives reduce the weight loss at room temperature, but the triol is much more effective than the other additives.

CLAIMS

1. The use of a diol or triol or a mixture of diols and/or triols as a corrosion inhibitor for organic or inorganic acids, or a mixture of acids.

2. The use according to claim 1 where the diol or triol or their mixture comprises 10-90% of the total mixture.

3. The use according to claim 1 and 2 where the triol is glycerol and the diol is glycol.

4. The use according to claim 1 to 3 where the mixture contains further corrosion inhibitors.

FIGURES

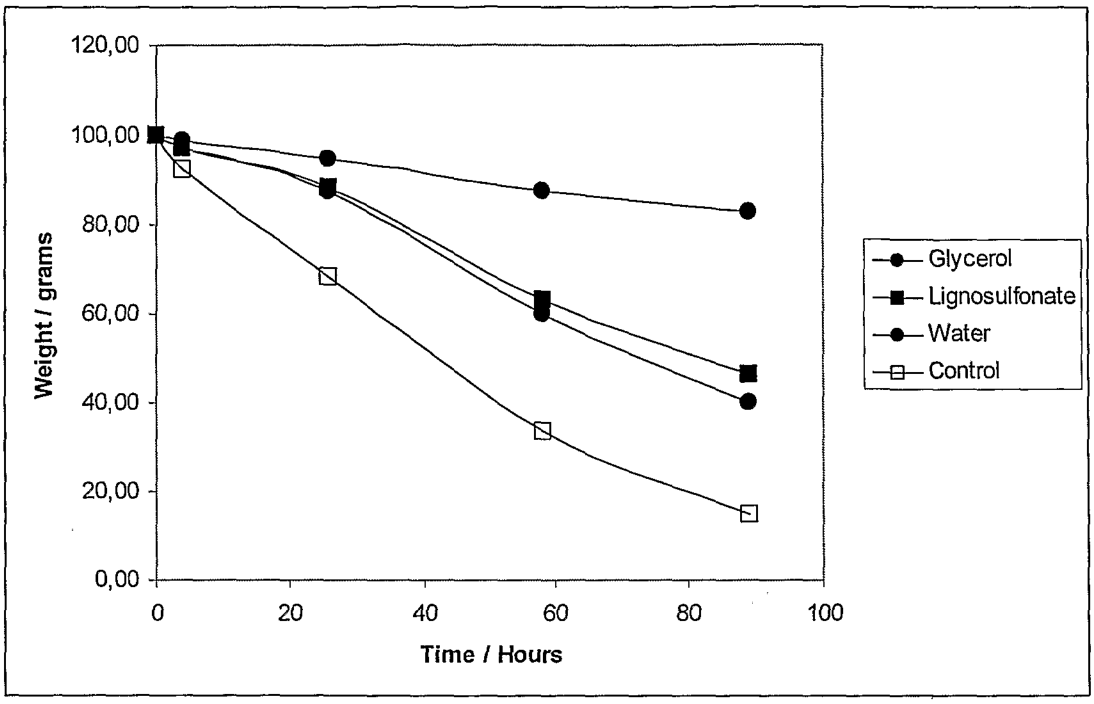

Figure 1: Evaporation loss versus time for different additives. Room temperature with stirring

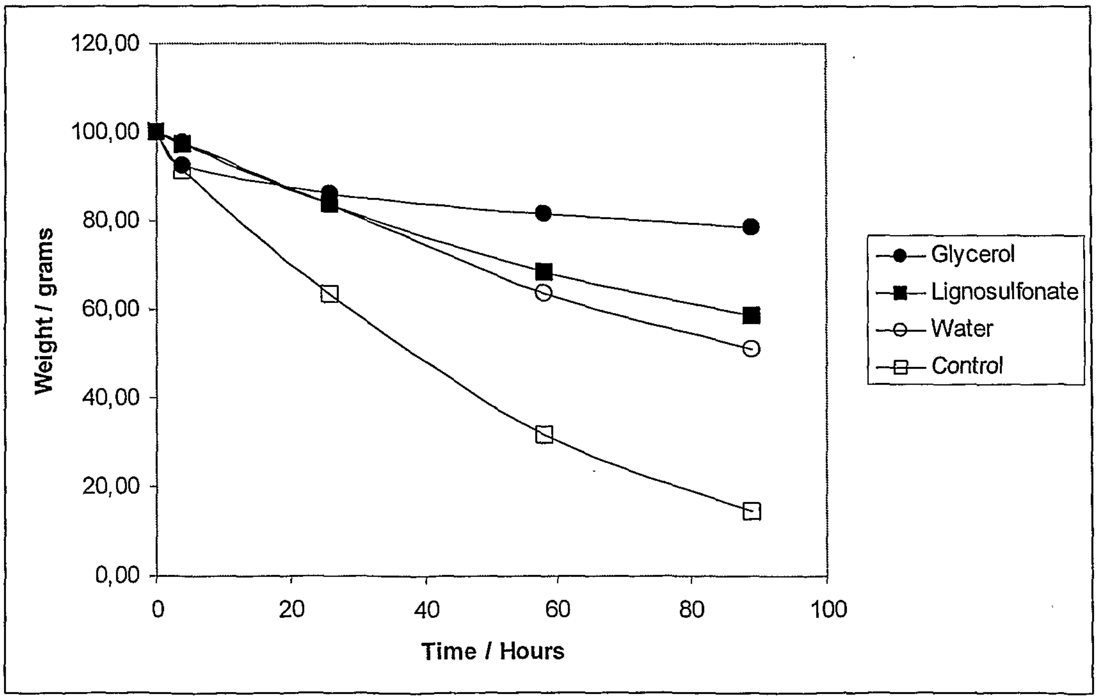

Figure 2: Evaporation loss versus time for different additives. Room temperature without stirring.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO2008/000329

A. CLASSIFICATION OF SUBJECT MATTER

IPC: see extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: C23F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL, WPI DATA, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 20030103865 A1 (LIBUTTI, BRUCE L. ET AL), 5 June 2003 (05.06.2003), paragraphs [0006], [0020] --	1-4
X	US 3772208 A (TEDESCHI, ROBERT J. ET AL), 13 November 1973 (13.11.1973), column 1, line 15 - line 21; column 1, line 30 - line 33 --	1-4
X	US 3004925 A (BURCH, ROBERT J.ET AL), 17 October 1961 (17.10.1961), column 1, line 10 - line 35 --	1-4

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

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"P" document published prior to the international filing date but later than the priority date claimed

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"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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 January 2009	09-01-2009

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2603622 A (BERGER, HEINRICH ET AL), 15 July 1952 (15.07.1952), column 1, line 7 - line 51; column 2, line 6 - line 11 --	1-4
X	EP 0192130 A2 (HENKEL CORPORATION), 27 August 1986 (27.08.1986), page 1, line 3 - line 7; page 2, line 28 - line 32 --	1-4
X	JP 2006348324 A, SUGIMURA KAGAKU KOGYO KK, 2006-12-28: (abstract) Retrieved from: EPODOC database -- --------	1-4

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Use the application number as username.
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Paper copies can be ordered at a cost of 50 SEK per copy from PRV InterPat (telephone number 08-782 28 85).

Cited literature, if any, will be enclosed in paper form.

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US	20030103865	A1	05/06/2003	US	6723257	B	20/04/2004
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