13146/88

COMMONWEALTH of AUSTRALIA

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

We   W. R. Grace & Co.-Conn.,   of
1114 Avenue of the Americas,
New York,
New York 10036,
United States of America,

APPLICATION ACCEPTED AND AMENDMENTS

ALLOWED _9 - 2 - 9c_

hereby apply for the grant of a Standard Patent for an invention entitled:

"CONTROL OF CORROSION IN AQUEOUS SYSTEMS"

which is described in the accompanying ~~provisional~~ complete specification.

Details of basic application(s):—

Number	Convention Country	Date
026,494	United States of America	16 March, 1987

The address for service is care of DAVIES & COLLISON, Patent Attorneys, of 1 Little Collins Street, Melbourne, in the State of Victoria, Commonwealth of Australia.

Dated this   16th   day of   February,   19 89.

To: THE COMMISSIONER OF PATENTS

....
(a member of the firm of DAVIES & COLLISON for and on behalf of the Applicant).

Davies & Collison, Melbourne and Canberra.

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

DECLARATION IN SUPPORT OF CONVENTION OR NON—CONVENTION APPLICATION FOR A PATENT

Insert title of invention.

In support of the Application made for a patent for an invention
entitled: "Control of corrosion in aqueous systems"

Insert full name(s) and address(es) of declarant(s) being the applicant(s) or person(s) authorized to sign on behalf of an applicant company.

I   William W. McDowell, Assistant Secretary,
Wg   Of W.R. Grace & Co.
     Of 1114 Avenue of the Americas,
     New York, New York 10036,
     United States of America.

Cross out whichever of paragraphs 1(a) or 1(b) does not apply

1(a) relates to application made by individual(s)

1(b) relates to application made by company; insert name of applicant company.

do solemnly and sincerely declare as follows :—

1. (a) ~~XXX~~ ~~Wxxxx~~ ~~xkexappdicanxxxxxXboxhexpherd~~

or (b) I am authorized by

   W.R. GRACE & CO.

the applicant............ for the patent to make this declaration on ~~their~~ its behalf.

Cross out whichever of paragraphs 2(a) or 2(b) does not apply

2(a) relates to application made by inventor(s)

2(b) relates to application made by company(s) or person(s) who are not inventor(s); insert full name(s) and address(es) of inventors.

2. (a) ~~XXX~~ ~~Wxxxx~~ ~~xHexactoxlXmprtxaxxxxxxxofxHxxmxextionx~~

or (b) Dionisio Guerrero Cuisia Of 6100 N. St. Louis
       Avenue, Chicago, Illinois 60659 and
       Chih Ming Hwa Of 1041 Nightingale Drive,
       Palatine, Illinois 60067 and
       Murrell Leon Salutsky Of 1950 Berkeley Road,
       Highland Park, Illinois 60035.
       All of the United States of America.

Xs
are the actual inventor....S....... of the invention and the facts upon which the applicant...........
is
xxx entitled to make the application are as follows :—

State manner in which applicant(s) derive title from inventor(s)

The actual inventors assigned the invention
to the said applicant.

Cross out paragraphs 3 and 4 for non-convention applications. For convention applications, insert basic country(s) followed by date(s) and basic applicant(s).

3.   The basic application,........... as defined by Section 141 of the Act ~~xxxx~~ was made
in United States of America. on the ...16th March, 1987................
by Dionisio Guerrero Cuisia, Chih Ming Hwa and
in Murrell Leon Salutsky... ~~xxxxx~~.....................
by ....
in .... on the ....
by..

4.   The basic application.......... referred to in paragraph 3 of this Declaration ~~xxxx~~ was
the first application.......... made in a Convention country in respect of the invention the subject
of the application.

Insert place and date of signature.

Declared at Columbia,   this   /7ᵗʰ day of November, 1987
          Maryland, USA

Signature of declarant(s) (no attestation required)

W. R. GRACE & CO.

William W McDowell (signature)

William W. McDowell, Jr.
Assistant Secretary

Note·   Initial all alterations.

DAVIES & COLLISON, MELBOURNE and CANBERRA.

(57) Claim

1. A method for control of corrosion of metals
in contact with system water in an aqueous system
comprising the step of adding to the system water an
effective amount of an oxygen scavenger selected from
the group of nitrones of the formula:

$$\begin{array}{c} R_1 \\ \diagdown \\ \diagup \\ R_2 \end{array} C = \overset{+}{N} \begin{array}{c} \diagup O^- \\ \diagdown \\ R_3 \end{array}$$
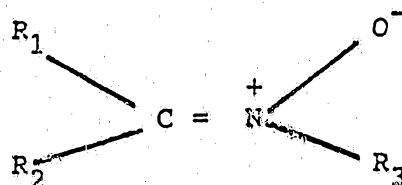
wherein R_1 and R_2 may be the same or different and are
each a member selected from the group consisting of
hydrogen and hydrocarbon radicals having between 1 and
10 carbon atoms, and R_3 is a hydrocarbon radical having
between 1 and 10 carbon atoms; or water soluble salts
thereof.

COMMONWEALTH OF AUSTRALIA

PATENT ACT 1952

COMPLETE SPECIFICATION

(ORIGINAL)

FOR OFFICE USE

CLASS   INT. CLASS

Application Number:
              Lodged:

Complete Specification Lodged:
              Accepted:
              Published:

Priority:

Related Art:

NAME OF APPLICANT: W.R. GRACE & CO. -CONN

ADDRESS OF APPLICANT: 1114 Avenue of the Americas,
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NAME(S) OF INVENTOR(S)   Dionisio Guerrero CUISIA

                Chih Ming HWA

                Murrell Leon SALUTSKY

ADDRESS FOR SERVICE: DAVIES & COLLISON, Patent Attorneys
                1 Little Collins Street, Melbourne, 3000.

COMPLETE SPECIFICATION FOR THE INVENTION ENTITLED:

   "CONTROL OF CORROSION IN AQUEOUS SYSTEMS"

The following statement is a full description of this invention,
including the best method of performing it known to us   :-

FIELD OF INVENTION

This invention relates to the addition of oxygen
scavengers to aqueous systems to reduce the corrosion
of metals that are in contact with water in the
systems, and more particularly, to the addition of a
composition comprising a nitrone or certain related
compounds to the system water of an aqueous system as
an oxygen scavenger to reduce corrosion of metal
surfaces in contact with the system water.

BACKGROUND OF THE INVENTION

In processes using aqueous solutions, corrosion of
metal surfaces may occur at various locations including
feed lines, heaters, steam lines, process tanks and
return lines. Dissolved oxygen in the water can be a
principal factor influencing this corrosion,
particularly where iron and steel are materials of
construction. The corrosion of the iron and steel
pipes, boilers, and economizers of conventional boiler
systems is a well known problem; and controlling the
presence of oxygen in boiler systems, particularly in
the feed water section, has received considerable
attention. Oxygen removal may be partially
accomplished by either vacuum or thermal deaeration, or
both. Complete removal of oxygen cannot be effected by
these means, however, and further removal by use of a
chemical scavenging agent, such as sodium sulfite, has
been a customary practice.

In recent times, the use of low pressure boilers (operating below about 150 psig) has been increasingly supplemented by use of boilers operating at moderate pressure (operating between about 150 psig and about 600 psig) and high pressure (operating above about 600 psig). As boiler operating temperatures and pressures have increased there has been particular interest in the performance of oxygen scavengers at these operating conditions. For example, use of sulphites at elevated temperatures and pressures may cause an increase in solids, and formation of sulfur dioxide and hydrogen sulfide, both of which can be a source of corrosion. Scavengers such as hydrazine, hydroquinone, and certain hydroxylamines have been found to perform satisfactorily in some circumstances. In other circumstances, the efficiency with which the scavenging proceeds has not been optimal. There is thus a continuing need for alternative oxygen scavengers which can be effectively used at elevated temperatures and pressures. Of particular value are single scavenging compounds which can be used in place of hydrazine.

Despite the reported toxicity of hydrazine, much recent research has concerned development of corrosion inhibitors using hydrazine together with various organic products. U.S. Patent No. 3,551,349 to Kallfass suggests using hydrazines in combination with activating amounts of various quinone compounds (including hydroxyl forms such as pyrocatechol and hydroquinone) and their derivatives, particularly those with hydrophilic substituents such as carboxylic acid and sulphonic acid. U.S. Patent No. 3,843,547 to

Kaufman et al. discloses a hydrazine-hydroxyl quinone combination in further combination with various aryl amine compounds; while U.S. Patent No. 3,983,048 to Schiessl et al. discloses a use of hydrazine along with a catalytic proportion of certain aryl amines, including sulfonated aryl amines. U.S. Patent No.'s 4,026,664 and 4,079,018 to Noack disclose hydrazine-based corrosion inhibitors which use organometallic complexes (including certain amino derivatives of carboxylic acids) as catalysts, and preferably quinone compounds (including hydroquinone) and their derivatives to render the compositions compatible with phosphonate scale control agents.

Other work has focused on nitrogen-containing compounds other than hydrazine such as various amines, hydroxylamines, or oximes. U.S. Patent 4,067,690 of Cuisia et al. discloses that hydroxylamine and certain derivatives thereof are highly effective oxygen scavengers in boiler water. The hydroxylamines may be catalyzed with any of a number of well-known catalysts used in sodium sulfite or hydrazine boiler water treatment. Alakli metal hydroxide, water soluble metal salts, hydroquinone, and benzoquinone are also useful catalysts. As disclosed in U.S. Patent No. 4,350,606 to Cuisia et al., the use of a hydroxylamine compound and a volatile, neutralizing amine such as cyclohexylamine, morpholine, diethylaminoethanol, dimethylpropanolamine, or 2-amino-2-methyl-1-propanol, inhibits corrosion in boiler systems caused by carbon dioxide and oxygen. Japanese Patent Document SHO

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57-204288 to Sato discloses using certain
hydroxylamines as de-oxidants in combination with
certain trivalent phenols, napthoquinones, and
anthraquinones or various derivatives thereof, as
5   activating agents. The invention may be practiced in
boiler related systems and activity is deemed
particularly significant in neutral and alkaline pH
ranges. U.K. Patent Application No. GB 2,157,670A by
Nemes et al. reveals advantageous use of hydroxylamines
10   together with neutralizing amines and a quinone, a
dihydroxybenzene, a diaminobenzene, or an
aminohydroxybenzene compound to scavenge oxygen and to
inhibit corrosion in boiler water and other aqueous
systems.
15   U.S. Patent No. 4,278,635 to Kerst discloses use
of various dihydroxy, diamino, and amino hydroxy
benzenes and their lower alkyl substituted derivatives
(including sulfonated napthalenes), and particularly
hydroquinone, as deoxygenating corrosion control agents
20   which compare favorably with other scavengers such as
hydrazine. Reaction rate increases with higher pH and
higher temperature are disclosed, as is use of the
invention in boiler systems. U.S. Patent No.'s
4,279,767; 4,289,645; and 4,487,708, all to Muccitelli,
25   are directed to use of hydroquinone as an oxygen
scavenger in combination with various compatible
amines. Addition of hydroquinone to boiler feedwater
together with certain neutralizing amines used to
neutralize carbon dioxide in the boiler condensate
30   system is disclosed. The systems preferably have
elevated temperatures and/or alkaline conditions.

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European Patent Publication No. 0054345 is directed to
use of certain aminophenol compounds to reduce oxygen
in aqueous medium such as boiler water. These
scavengers are deemed to outperform hydrazine in
simulated feedwater conditions and are preferably used
in alkaline pH.

U.S. Patent No. 4,487,745 to Weiss et al. is
directed to the use of certain oximes to remove
dissolved oxygen from aqueous systems such as steam
generating systems, and to thereby inhibit the
corrosion of metal surfaces. U.S. Patent No. 4,269,717
to Slovinsky is directed to similar use of
carbohydrazide and discloses that certain scavengers
show activity comparable to hydrazine while other
similar compounds do not. U.S. Patent No. 4,399,098 to
Cuisia discloses use of semicarbazide and its salts as
oxygen scavengers in aqueous systems such as boiler
water systems to reduce corrosion from dissolved
oxygen. U.S. Patent No. 4,479,917 to Rothgery et al.
is directed to an oxygen-scavenging, corrosion-
inhibiting agent for fluidic systems comprising certain
aminoguanidine compounds. U.S. Patent No. 2,170,596 to
Quiggle describes oxygen-absorbing solutions using
catalysts such as amidol, para amido phenol, and
certain amino-anthraquinones together with reducing
agents such as sulfides.

It is well known that a nitrone may be prepared by
the reaction of a hydroxylamine, particularly a mono
N-substituted hydroxylamine, with an aldehyde or a
ketone. It is also known that alkylation of oximes
using agents such as alkyl halides or sulfates yields
nitrones as well as oxime ethers, the relative yield of

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each depending on the reaction conditions and the
nature of the reagents (including the configuration of
the oxime). U.S. Patent No. 4,596,874 to Murahashi et
al. describes nitrone synthesis by reacting certain

5   secondary amines with a peroxide in the presence of a
catalyst.

SUMMARY OF THE INVENTION

10   We have found that the addition of nitrones or
their water soluble salts to the system water of
aqueous systems, including boiler and steam condensate
systems, inhibits the corrosion of metal in contact
with the system water by removing oxygen in the system.

15   The invention herein described surprisingly promotes
the rapid scavenging of oxygen in aqueous systems, such
as boiler water systems, containing dissolved air
and/or oxygen. The invention is especially suited for
aqueous systems such as boiler and steam condensate

20   systems wherein the system liquid or steam consists
essentially of water and oxygen. Indeed, the
efficiency of oxygen scavenging achieved by using the
additives, and the effectiveness of the additives at
conditions found within boiler systems, makes boiler

25   system use particularly advantageous.
        Accordingly, it is an object of this invention to
provide a method to inhibit corrosion of metals in
contact with aqueous solutions.
        It is another object of this invention to remove

30   oxygen from boiler system water.

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It is still another object of this invention to remove oxygen from steam and its condensate.

These and other objects and advantages of the present invention will become apparent from the detailed description of the invention which follows.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic view of one apparatus used to test oxygen scavenging.

DETAILED DESCRIPTION

Nitrones are used in accordance with this invention to effectively scavenge oxygen from an aqueous system so that corrosion of metals in contact with the system water is inhibited. In general, the corrosion inhibiting agents used in this invention include a nitrone having the structural formula:

$$R_1 \diagdown \atop R_2 \diagup C = \overset{+}{N} {\diagup O^- \atop \diagdown R_3}$$
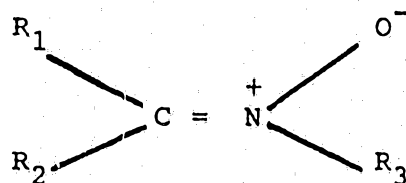
R_1 and R_2 may be the same or different and are each selected from the group consisting of hydrogen and hydrocarbon radicals having between one and ten carbon atoms. R_3 is a hydrocarbon radical having between one and ten carbon atoms. R_1, R_2, and R_3 may all be selected from alkyl groups (saturated or unsaturated),

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cycloalkyl groups, aryl groups, or aralkyl groups.
Examples of said alkyl groups include methyl, ethyl,
n-propyl, isopropyl, n-butyl, n-pentyl, n-hexyl,
n-heptyl, n-octyl, n-nonyl, n-decyl, and the various
n-hexenyl, n-heptenyl, n-octenyl, n-nonenyl and
n-decenyl radicals. Examples of said cycloalkyl, aryl,
and aralkyl groups, respectively, include cyclohexyl,
phenyl, and tolyl radicals. The preferred hydrocarbon
radicals are groups which have between one and seven
carbons. Examples of preferred compounds are thus
formaldehyde isopropylnitrone; formaldehyde ethyl-
nitrone, formaldehyde methylnitrone, acetaldehyde
isopropylnitrone, acetaldehyde propylnitrone,
acetaldehyde ethylnitrone, acetaldehyde methylnitrone,
acetone isopropylnitrone, acetone propylnitrone,
acetone ethylnitrone, acetone methylnitrone, acetone
n-butylnitrone, acetone benzylnitrone, formaldehyde
n-hexylnitrone, methyl ethyl ketone ethylnitrone,
formaldehyde cyclohexylnitrone, isobutyraldehyde
isopropylnitrone, isobutyraldehyde ethylnitrone,
n-butyraldehyde isoproylnitrone, n-butyraldehyde
ethylnitrone, and n-butyraldehyde propylnitrone. These
preferred compounds include formaldehyde alkyl nitrones
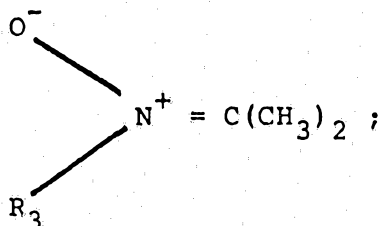having the general structural formula:
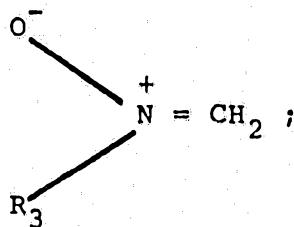
$$\underset{R_3}{\overset{O^-}{\diagdown}}N^+ = CH_2 \; ;$$

acetaldehyde alkyl nitrones having the general
structural formula:

$$O^- \diagdown \atop R_3 \diagup N^+ = CH(CH_3) \; ;$$
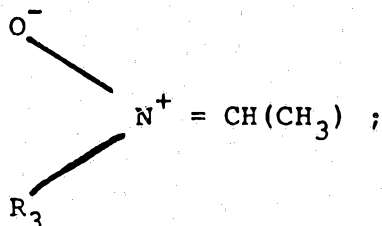
and acetone alkyl nitrones having the general
structural formula:

$$O^- \diagdown \atop R_3 \diagup N^+ = C(CH_3)_2 \; ;$$

wherein R_3 is a saturated or unsaturated alkyl having
between one and ten, and preferably between one and
seven, carbon atoms. Low molecular weight embodiments
of formaldehyde alkyl nitrones, acetaldehyde alkyl
nitrones, and acetone alkyl nitrones such as those
where R_3 is methyl, ethyl, propyl, or isopropyl are
particularly useful where higher volatility is desired.
Water soluble salts of the nitrones used in accordance
with this invention may also be used.

The use of nitrones as oxygen scavengers may be
practiced in various water systems, such as
recirculating heating or cooling systems. We have
found that they are particularly suited for use as
oxygen scavenging additives to boiler related systems,

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such as, for example, boiler feedwater and boiler water
where the water is preferably maintained at a pH
between about 7 and about 12, most preferably from
about 8 to about 11. One suggested use is for

5   treatment of water in a dormant boiler wherein the
nitrone may be added along with sufficient amounts of
alkaline agents such as sodium hydroxide to raise the
pH to within the desired range. The higher alkalinity
also aids in corrosion inhibition. In boiler water

10   systems, corrosion may occur in feed lines, heaters,
economizers, boilers, steam lines, and return lines;
and the invention is intended for broad use in any
boiler water system (i.e. at pressures in the range of
0 to 1000 psig or higher). The volatility of nitrones

15   included within this invention, especially those having
relatively low molecular weights, also makes them
useful in steam and steam condensate systems where
addition may be made to either the steam or to its
condensate. Oxygen scavenging is particularly

20   effective in systems where the water reaches elevated
temperatures, above say 190 degrees Fahrenheit.
Indeed, inasmuch as nitrones perform effectively at
higher pressures and temperatures, they are considered
particularly suited for boiler water systems which

25   operate at temperatures in the range of about 298°F to
about 637°F and at pressures in the range of about 50
psig to 2000 psig. They are also considered effective
scavengers for boiler systems which operate at even
higher temperatures and pressures. The metal surfaces

30   exposed to these conditions are generally iron and steel.
Practice of the invention will become further
apparent from the following non-limiting examples.

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EXAMPLE I

The oxygen scavenging activity of the chemicals was evaluated in an experimental boiler. This experimental boiler has been described previously in the proceedings of the Fifteenth Annual Water Conference, Engineers Society of Western Pennsylvania, pages 87-102 (1954). Essentially, it consists of a vertical steel tube fitted with three external heating loops extending from near the bottom and discharging near the center of the central tube. Boiler water circulates through each heating loop from bottom to top and steam is withdrawn from the top of the vertical tube. The heating source in each loop consists of an electrical fire-rod unit transferring heat indirectly through the walls of a heating tube.

The feedwater was saturated with oxygen by continuous aeration maintaining about 8 to 9 parts per million (ppm) of dissolved oxygen. This feedwater contained a total hardness of approximately 10 ppm (as $CaCO_3$). Typical boiler water treatment chemicals such as sodium hydroxide (caustic soda) and disodium phosphate for alkalinity and calcium hardness control were added to the water in the boiler. The boiler water pH ranged from 10.8 to 11.2. Feedwater passed into the boiler where it was heated to a temperature of about 448°F under a pressure of about 400 psig. After steam formation, the steam was condensed through a heat exchanger. The condensate, which had a temperature of approximately 55°F, was then passed through a chamber containing a standard oxygen probe. The dissolved oxygen in the condensate was measured in the chamber to

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determine the effectiveness of oxygen removal within the system.

Boiler water was fed through the system without addition of any oxygen scavenger until a constant dissolved oxygen reading was observed in the condensate. Once the base dissolved oxygen level in the condensate was established, formaldehyde isopropylnitrone was added as the sole oxygen scavenger to the boiler feedwater at a dosage of 80 parts per million (ppm). The dissolved oxygen level in the condensate was then monitored to determine a final level by which the effectiveness of the nitrone could be determined.

A second run was made using formaldehyde ethylnitrone in place of formaldehyde isopropylnitrone. After a base dissolved oxygen level in the condensate was established, formaldehyde ethylnitrone was added to the feedwater at a dosage of 80 ppm. The final level of the oxygen in the condensate was then measured to determine the effectiveness of the nitrone in the system.

A third run was made using hydrazine. After a base dissolved oxygen level in the condensate was established, hydrazine was added to the feedwater at a dosage of 80 ppm. The final level of oxygen in the condensate was then measured to determine the effectiveness of the hydrazine in the system.

A fourth run was made using sodium sulfite. After a base dissolved oxygen level in the condensate was established, sodium sulfite was added to the feedwater at a dosage of 80 ppm. The final level of oxygen in the condensate was then measured to determine the effectiveness of the sulfite in the system.

The results of these runs are summarized in Table I.

TABLE I

Run No.	Oxygen Scavenger	Base Level of Dissolved Oxygen in Condensate (ppm)	Dosage of Oxygen Scavenger		Final Level of Dissolved Oxygen in Condensate (ppm)	Reduction in Dissolved Oxygen	
			moles per liter	parts per million		parts per million	percent
1	Formaldehyde Isopropylnitrone	3.2	.00092	80	0.3	2.9	90.6
2	Formaldehyde Ethylnitrone	3.6	.0011	80	0.9	2.7	75.0
3	Hydrazine	2.7	.0025	80	0.1	2.6	96.3
4	Sodium Sulfite	2.7	.000635	80	0.1	2.6	96.3

The results shown in Table I indicate that
nitrones were effective oxygen scavengers in the boiler
system. It is evident that nitrones may be utilized as
an oxygen scavengers in moderate and high pressure
5   boiler systems. The iron and steel components
typically found in these systems can thus be
effectively protected from oxygen-related corrosion.

<center>EXAMPLE II</center>

10

The oxygen scavenging activity of nitrones were
also evaluated and compared to that of hydrazine under
simulated boiler feedwater conditions. The apparatus
used for this evaluation is depicted schematically in
15   Fig. 1. The apparatus (10) comprises a peristaltic
pump (11) which is used for circulating water
throughout the system, pump inlet tubing (12) and pump
outlet tubing (13). A polyethylene fill-bottle (14) is
connected with the inlet tubing (12) and is used to
20   feed system water into the apparatus. A valve (15),
which may be selectively opened and closed, is provided
between the fill-bottle (14) and the inlet tubing (12)
and is used to control flow therebetween. A
temperature measurement chamber (16) is positioned
25   within the pump inlet tubing (12) and contains a
thermometer (17) used for monitoring the water
temperature. The system water is drawn through the
inlet tubing (12), into the pump (11), and then is
pumped via the pump outlet tubing (13) into a glass
30   sampling chamber (18). The sampling chamber (18)
contains a pH probe (19) and a dissolved oxygen probe

<center>- 15 -</center>

(20). The pH probe (19) is operably connected to a pH
meter (21) used for displaying and monitoring the
system water pH; and the dissolved oxygen probe (20) is
operably connected to a dissolved oxygen meter (22)
used for displaying and monitoring the system water
dissolved oxygen level, as well as to a recorder (23)
used for continuously recording the dissolved oxygen
level in the system water. Tubing (24) is provided for
directing system water from the glass sampling chamber
(18) to the one liter stainless steel preheat reactor
(25), known in the laboratory as a "Parr vessel." A
glass chemical inlet chamber (26) is positioned within
the tubing (24) and may be fitted with a rubber septum
(not shown) through which a chemical solution of oxygen
scavenger may be injected. The preheat reactor (25)
contains a heating element (not shown) which may be
activated to preheat the system water. Water forced
out of the preheat reactor (25) by operation of the
pump (11) is directed through tubing (27) to a two
liter stainless steel heating reactor (28) where the
system water is heated to its highest temperature. A
heating element and a thermostat (not shown) are
provided for maintaining the water temperature in the
heating reactor (28) relatively constant. The water
from the heating reactor (28) passes through tubing
(29) into a water cooled heat exchanger (30) which
cools the system water to a range of about 55°F to
60°F. System water from the heat exchanger (30) is
then recirculated into the pump inlet tubing (12).
Thus, while the system water may be heated to elevated
temperatures in the preheat reactor (25) and heating

reactor (28), the recirculated water passing through
the pump (11) and into the sampling chamber (18) may be
kept at a relatively constant temperature conducive to
accurate probe operation. The full capacity of the
apparatus (10) is about 4.5 liters while the pumping
rate of pump (11) is about 0.30 to 0.35 liters per
minute.

The oxygen scavenging activities of nitrones and
hydrazine were each investigated at system water
conditions of 190°F and pH 8.5. In each run distilled
water saturated with oxygen (about 8 to 9 ppm) and
adjusted to the requisite pH with sodium hydroxide, was
fed into the system through the polyethylene
fill-bottle (14). The system was filled to its
capacity with water to the substantial exclusion of
air, and the water was heated using the preheat reactor
(25) and heating reactor (28) until the steady state
was achieved at which the temperature of system water
leaving the heating reactor (28), as controlled by the
thermostat therein, was about 190°F, and the
temperature of the system water leaving the heat
exchanger (30) as measured by thermometer (17) was from
about 55°F to 60°F. During this period, gas was
allowed to exit from the system through the fill-bottle
(14) and the chemical inlet chamber (26); and the
dissolved oxygen level in the circulating water was
allowed to equilibrate. Recirculation continued in
each run until the oxygen level in the system water
remained constant for at least 30 minutes. Once the
initial oxygen reading was established, the system was
effectively closed to the atmosphere and the oxygen

scavenger was injected through a rubber septum fitted
in the chemical inlet chamber (26). Recycling
continued for 30 minutes, during which time the oxygen
level in the sampling chamber (18) was monitored. The
5   results given in Table II below were obtained on
separate runs using hydrazine (Run 12) and various
dosages of the nitrones formaldehyde isopropylnitrone
(Runs 5 and 6), formaldehyde ethylnitrone (Run 7),
acetaldehyde isopropylnitrone (Run 8), acetaldehyde
10   ethylnitrone (Run 9), acetone isopropylnitrone (Run
10), and acetone ethylnitrone (Run 11).

TABLE II

Run No.	Oxygen Scavenger	Base Level of Dissolved Oxygen in Condensate (ppm)	Dosage of Oxygen Scavenger (moles per mole O_2)	Final Level of Dissolved Oxygen in Condensate (ppm)	Reduction in Dissolved Oxygen	
					parts per million	percent
5	Formaldehyde Isopropylnitrone	3.5	5:1	1.9	1.6	45.7
6	Formaldehyde Isopropylnitrone	3.4	10:1	1.3	2.1	61.8
7	Formaldehyde Ethylnitrone	3.5	4:1	1.5	2.0	57.1
8	Acetaldehyde Isopropylnitrone	5.2	4:1	1.2	4.0	76.9
9	Acetaldehyde Ethylnitrone	4.1	5:1	1.6	2.5	61.0
10	Acetone Isopropylnitrone	3.2	4:1	0.7	2.5	78.1
11	Acetone Ethylnitrone	4.5	4:1	1.5	3.0	66.7
12	Hydrazine	3.4	3:1	1.2	2.2	64.7

The results shown in Table II indicate that
nitrones were effective oxygen scavengers in the system
water. It is evident that nitrones may be
advantageously utilized as an oxygen scavenger in
5 feedwater systems of moderate and high temperature
boilers. The iron and steel components typically found
in these systems can thus be effectively protected from
oxygen-related corrosion.

The process of this invention for inhibiting
10 corrosion of metal surfaces in contact with the system
water of an aqueous system by scavenging oxygen from
the system water comprises adding to the system water
an effective amount of at least one nitrone. The
preferred dosage range of nitrone is generally from
15 about 0.01 ppm to about 10,000 ppm. Concentrations
toward the lower end of this range, say up to about 200
ppm, are most practical in systems where additional
means of oxygen removal are also provided such as, for
example, boiler water systems and the like having
20 deaerators in which mechanical deaeration is
practiced. Concentrations toward the upper end of this
range, say about 20 ppm and above, are most practical
where slug dosages are made to a system such as, for
example, a recirculating hot water system, to provide
25 residual nitrone over a long time period. The most
preferred dosage range is generally from about 0.05 ppm
to about 1,000 ppm. Use of nitrones is not confined to
low, moderate or high pressure boiler systems, but may
be utilized in a wide variety of other systems where
30 aqueous solutions containing dissolved air and/or
oxygen are in contact with metal surfaces. The precise

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dosage used in each system will be somewhat dependent
on the specific nitrone and the particular system and
the water characteristics therein. The preferred
system liquid (which may contain small amounts of
5 certain additives normally used in systems such as
boiler water systems for control of corrosion, scaling,
sedimentation, pH, hardness and the like) consists
essentially of water containing dissolved oxygen.
Likewise, where the nitrones are used to protect steam
10 systems, the preferred steam composition (which may
contain other gases normally found in air, as well as
other system volatiles) consists essentially of water
and oxygen. In systems where addition is made to
system water which will not be further aerated before
15 it contacts the metal surfaces to be protected, a mole
ratio of nitrone to oxygen in the system is preferably
between about 0.1:1 to about 1,000:1; most preferably
between about 0.5:1 to about 50:1. Preferably
the temperature of the system water reaches the range
20 of about 40°F to about 700°F as scavenging proceeds,
most preferably between about 60°F and about 600°F.

It is generally economical, especially where the
systems are not operated at elevated temperatures, that
the system water have a pH greater than about 5 as
25 oxygen scavenging proceeds; preferably between about 7
and about 12; most preferably from about 8 to about 11.

The preferred pH may be maintained by conventional
means such as adding alkaline agents. Preferred
conventional agents include sodium hydroxide, potassium
30 hydroxide, sodium carbonate, potassium carbonate, and
phosphate salts of high alkalinity, such as disodium

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phosphate, and trisodium phosphate (especially trisodium phosphate). In boiler water systems, sodium hydroxide and potassium hydroxide are generally preferred over sodium carbonate and potassium carbonate because of the known potential for carbonates to contribute to carbon dioxide induced corrosion.

The oxygen scavengers are preferably added directly to the system water as nitrones. However, compositions which, upon being added to an aqueous system, yield an oxygen scavenger consisting essentially of nitrones would of course provide similar corrosion protection and are considered within the scope of our findings.

The nitrone compositions employed in the process of this invention can typically be added to the system water by conventional bypass feeders using briquettes containing the additives, by feeding the compounds as dry powder mixtures to the water, or by feeding the treatment compounds as an aqueous feed solution. Feed solutions, when used, preferably contain from about 0.5 to about 95 percent by weight of nitrone oxygen scavenger; most preferably from about 5 to about 60 weight percent thereof. Where, as in many boiler systems, make-up water is added to the aqueous solution, calibrated injecters can be employed to deliver predetermined amounts of the nitrones, periodically or continuously, to the aqueous solution via the make-up water line. While the scavengers may be added at locations throughout the system, the addition is preferably made at a location where there is little opportunity for additional aeration of the

solution before it contacts the metal components to be
protected. For example, in boiler systems, addition is
preferably made to the feedwater at a location where
the feedwater will not be exposed to substantial

5   aeration before it enters the boiler. Examples of such
locations might include the feedwater line itself, or
depending upon the boiler system design, the return
condensate lines, make-up water lines, or the storage
section of deaerators.

10   The examples describe particular embodiments of
the invention. Other embodiments will be apparent to
those skilled in the art from a consideration of the
specification or practice of the invention disclosed
herein. It is understood that modifications and

15   variations may be practiced without departing from the
spirit and scope of the novel concepts of this
invention. It is further understood that the invention
is not confined to the particular formulations and
examples herein illustrated, but it embraces such

20   modified forms thereof as come within the scope of the
following claims.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1.   A method for control of corrosion of metals
in contact with system water in an aqueous system
comprising the step of adding to the system water an
effective amount of an oxygen scavenger selected from
the group of nitrones of the formula:

$$\begin{array}{c} R_1 \\ \diagdown \\ \diagup \\ R_2 \end{array} C = \overset{+}{N} \begin{array}{c} \diagup O^- \\ \\ \diagdown R_3 \end{array}$$
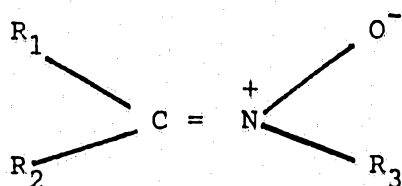
wherein R_1 and R_2 may be the same or different and are
each a member selected from the group consisting of
hydrogen and hydrocarbon radicals having between 1 and
10 carbon atoms, and R_3 is a hydrocarbon radical having
between 1 and 10 carbon atoms; or water soluble salts
thereof.

2.   The method of Claim 1 wherein R_1 and R_2 are
each independently selected from a group consisting of
saturated or unsaturated alkyl groups having between 1
and 7 carbons and hydrogen.

3.   The method of Claim 2 wherein R_3 is a
saturated or unsaturated alkyl having between 1 and 7
carbons.

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4.   The method of Claim 1 wherein R_1, R_2, and R_3
are all selected from the groups consisting of a
saturated and unsaturated alkyl groups, cycloalkyl
groups, aryl groups, and aralkyl groups.

5.   The method of Claim 1 wherein the scavenger
is added at a dosage of between ~~about~~ 0.01 ppm and
~~about~~ 10,000 ppm.

6.   The method of Claim 1 wherein the scavenger
added is a formaldehyde alkyl nitrone, an acetaldehyde
alkyl nitrone, an acetone alkyl nitrone, or a water
soluble salt thereof and wherein R_3 is a saturated or
unsaturated alkyl having between 1 and 7 carbons.

7.   The method of Claim 6 wherein the scavenger
is added at a dosage between ~~about~~ 0.01 ppm and ~~about~~
10,000 ppm.

8.   The method of Claim 6 wherein R_3 is selected
from a group consisting of methyl, ethyl, propyl, and
isopropyl radicals.

9.   The method of Claim 1 wherein the scavenger
comprises formaldehyde isopropylnitrone, formaldehyde
ethylnitrone, acetaldehyde isopropylnitrone,
acetaldehyde ethylnitrone, acetone isopropylnitrone,
acetone ethylnitrone, or a water soluble salt thereof.

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10. The method of Claim 1 wherein the system
water is maintained at a pH within the range of about 7
to about 12.

11. The method of Claim 10 wherein the
temperature of the system water reaches the range of
about 40°F to about 700°F as scavenging proceeds.

12. The method of Claim 1 wherein addition is
made to system water which will not be further aerated
before it contacts the metal surfaces, and wherein the
mole ratio of nitrones to oxygen dissolved in the
system water is from about 0.1:1 to about 1,000:1.

13. The method of Claim 1 particularly adapted
for use in boiler and steam condensate systems to
protect the system metals in contact with system liquid
or steam wherein the system liquid or steam consists
essentially of water and oxygen; and wherein the oxygen
scavenger is added directly to the system as nitrone.

14. The method of Claim 13 wherein the scavenger
is added at a location wherein there is no substantial
further aeration of the water before it contacts the
metal surfaces to be protected, and in a mole ratio of
oxygen in the boiler feedwater of from about 0.1:1 to
about 1,000:1.

15. The method of Claim 14 wherein the scavenger
is added in a mole ratio to oxygen in the boiler
feedwater of about 0.5:1 to about 50:1.

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1   16. The method of Claim 14 wherein R_1 and R_2 are each independently selected from a group consisting of

3 saturated and unsaturated alkyl groups having between 1 and 10 carbons and hydrogen; and wherein R_3 is selected

5 from the group consisting of saturated or unsaturated alkyl having between 1 and 10 carbons.

1   17. The method of Claim 13 wherein the scavenger comprises a formaldehyde alkyl nitrone, an acetaldehyde

3 alkyl nitrone, an acetone alkyl nitrone, or a water soluble salt thereof, wherein R_3 is a saturated or

5 unsaturated alkyl having between 1 and 10 carbons; and wherein the nitrone is added at a dosage of from ~~about~~

7 0.01 ppm to ~~about~~ 10,000 ppm.

1   18. The method of Claim 17 wherein R_3 is selected from a group consisting of methyl, ethyl, propyl, and

3 isopropyl radicals.

1   19. The method of Claim 13 wherein addition is made to the boiler feedwater; and wherein the feedwater

3 is adjusted to a pH of between ~~about~~ 7 to ~~about~~ 12.

1   20. The method of Claim 13 wherein the system contains steam and addition is made to the steam.

1   21. The method of Claim 1 particularly adapted for use in boiler systems operating at pressures of at

3 least about 50 psig and temperatures of at least about 298°F to protect the iron and steel boiler system

5 components in contact with the boiler water, wherein the oxygen scavenger is added to the boiler water.

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22. The method of Claim 21 wherein the boiler system has a deaerator and deaeration is practiced.

23. The method of Claim 22 wherein the concentration of nitrone is between ~~about~~ 0.01 ppm and ~~about~~ 200 ppm.

24. The method of Claim 23 wherein the scavenger is added at a location wherein there is no substantial further aeration of the water before it enters the boiler in a mole ratio to oxygen in the boiler feedwater of from ~~about~~ 0.1:1 to ~~about~~ 1,000:1.

25. The method of Claim 24 wherein addition is made to the boiler feedwater, and the feedwater is adjusted to a pH of between ~~about~~ 7 and ~~about~~ 12.

26. The method of Claim 21 wherein the scavenger is added at a dosage between ~~about~~ 0.01 ppm to ~~about~~ 10,000 ppm.

27. The method of Claim 26 wherein the scavenger comprises a formaldehyde alkyl nitrone, an acetaldehyde alkyl nitrone, an acetone alkyl nitrone, or a water soluble salt thereof, and wherein R_3 is a saturated or unsaturated alkyl having between 1 and 10 carbons.

28. The method of Claim 27 wherein R_3 is selected from a group consisting of methyl, ethyl, propyl and isopropyl radicals; and wherein the pH of the system is maintained between ~~about~~ 7 and ~~about~~ 12.

1   29. The method of Claim 27 wherein the mole ratio
of nitrone to oxygen dissolved in the solution is
3   between ~~about~~ 0.5:1 and ~~about~~ 50:1; the boiler water pH
is maintained at a pH of between ~~about~~ 7 and 12; and
5   the dosage of nitrone is between ~~about~~ 0.05 ppm and
1,000 ppm.

1   30. The method of Claim 26 wherein the boiler
system reaches operating pressures between ~~about~~ 50
3   psig and ~~about~~ 2000 psig and operating temperatures
between ~~about~~ 298°F and about 637°F as scavenging
5   proceeds.

1   31. The method of Claim 26 wherein the boiler
water is maintained at a pH of between about 7 and 12;
3   and wherein the scavenger comprises formaldehyde
isopropylnitrone, formaldehyde ethylnitrone,
5   acetaldehyde isopropylnitrone, acetaldehyde
ethylnitrone, acetone isopropylnitrone, acetone
7   ethylnitrone, or a water soluble salt thereof.

1   32. The method of Claim 31 wherein the mole ratio
of nitrone to oxygen dissolved in the solution is
3   between ~~about~~ 0.1:1 and ~~about~~ 1,000:1; and the dosage
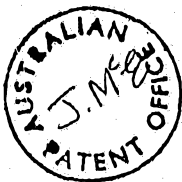of nitrone is between ~~about~~ 0.05 ppm and 1,000 ppm.

         33. A method according to claim 1, substantially
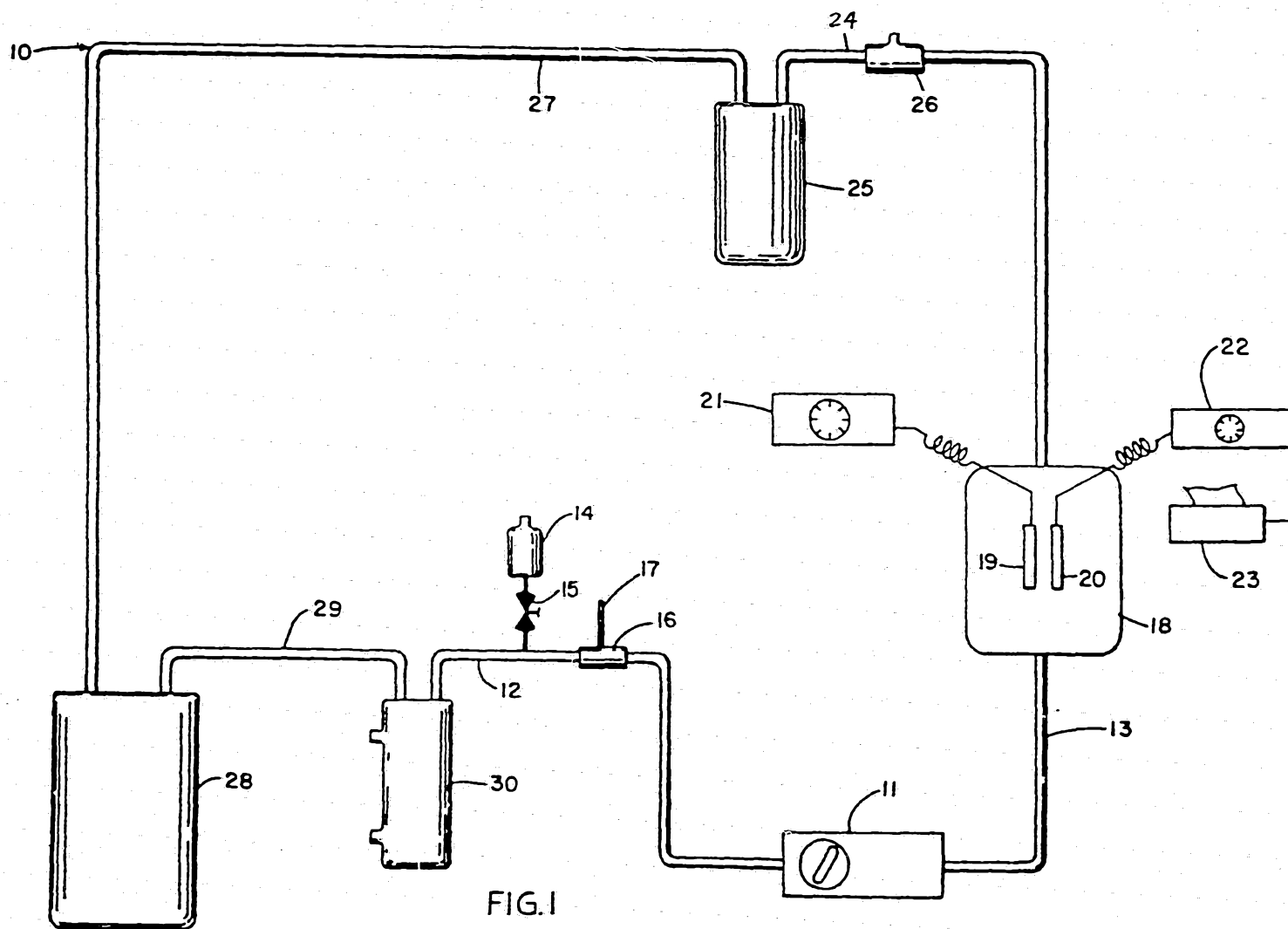as hereinbefore described with reference to the Examples
and/or drawing.

34. The steps, features, compositions and compounds referred to or indicated in the specification and/or claims of this application, individually or collectively, and any and all combinations of any two or more of said steps or features.

Dated this 16th day of March 1988

W.R. GRACE & CO., ~ CONN
By its Patent Attorneys,
DAVIES & COLLISON.

FIG.1