

605588

FORM 1

SPRUSON & FERGUSON

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

DuBois Chemicals, Inc., of 1100 DuBois Tower, Cincinnati, Ohio, 45202, UNITED STATES OF AMERICA, hereby apply for the grant of a standard patent for an invention entitled:

Oxygen Scavenger for Boiler Water and Method of Use

which is described in the accompanying complete specification.

Details of basic application(s):-

Basic Applic. No: Country:

131754

US

Application Date:

11 December 1987

The address for service is:-

Spruson & Ferguson
Patent Attorneys
Level 33 St Martins Tower
31 Market Street
Sydney New South Wales Australia

DATED this TWENTY SIXTH day of MAY 1988

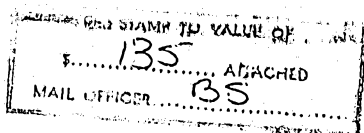
DuBois Chemicals, Inc.

By:

H. J. Anderson

Registered Patent Attorney

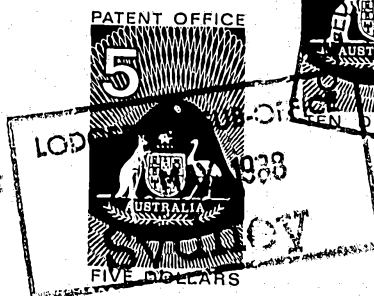
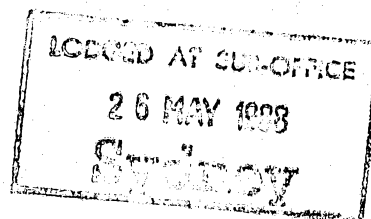
TO: THE COMMISSIONER OF PATENTS
OUR REF: 58345
S&F CODE: 64180



5845/2

APPLICATION ACCEPTED AND AMENDMENTS

ALLOWED 23-10-90



COMMONWEALTH OF AUSTRALIA

THE PATENTS ACT 1952

DECLARATION IN SUPPORT OF A
CONVENTION APPLICATION FOR A PATENTAUSTRALIA
CONVENTION
STANDARD
& PETTY PATENT
DECLARATION
SFP4In support of the Convention Application made for a
patent for an invention entitled:

Title of Invention

OXYGEN SCAVENGER FOR BOILER WATER AND METHOD OF USE

Full name(s) and
address(es) of
Declarant(s)I/~~We~~ Mark J. Hanket, Vice President
DuBois Chemicals, Inc.of 1100 DuBois Tower
Cincinnati, Ohio 45202
United States of America

do solemnly and sincerely declare as follows:--

Full name(s) of
Applicant(s)1. ~~I am/We are the applicant(s) for the patent~~

(or, in the case of an application by a body corporate)

1. ~~I am/We are authorised by~~ I am authorised byDuBois Chemicals, Inc.
the applicant(s) for the patent to make this declaration on
its/their behalf.2. The basic application(s) as defined by Section 141 of the
Act was/were made

Basic Country(ies)

in United States of America

Priority Date(s)

on December 11, 1987

Basic Applicant(s)

by Ronald J. Christensen and Lyle H. Steimel

Full name(s) and
address(es) of
inventor(s)3. ~~I am/We are the actual inventor(s) of the invention referred
to in the basic application(s)~~

(or where a person other than the inventor is the applicant)

3. Ronald J. Christensen Lyle H. Steimel
8747 Tanagerwoods Drive 1117 Imprint
Montgomery, Ohio and Forest Park, Ohio
of both in the United States of America

(respectively)

is/are the actual inventor(s) of the invention and the facts upon
which the applicant(s) is/~~are~~ entitled to make the application are
as follows:

the applicant is the assignee of the actual inventors

Set out how Applicant(s)
derive title from actual
inventor(s) e.g. The
Applicant(s) is/are the
assignee(s) of the
invention from the
inventor(s)4. The basic application(s) referred to in paragraph 2 of this
Declaration was/were the first application(s) made in a Convention
country in respect of the invention(s) the subject of the application.Declared at Cincinnati, OH this 29th day of April 19 88
U.S.A.Signature of Declarant(s)
Mark J. Hanket
Vice President

11/81

To: The Commissioner of Patents

(12) PATENT ABRIDGMENT **(11) Document No. AU-B-16673/88**
(19) AUSTRALIAN PATENT OFFICE **(10) Acceptance No. 605588**

(54) Title
OXYGEN SCAVENGER FOR BOILER WATER AND METHOD OF USE

International Patent Classification(s)
(51)⁴ **C02F 001/58** **C07C 091/06**

(21) Application No. : **16673/88** (22) Application Date : **26.05.88**

(30) Priority Data

(31) Number	(32) Date	(33) Country
131754	11.12.87	US UNITED STATES OF AMERICA

(43) Publication Date : **15.06.89**

(44) Publication Date of Accepted Application : **17.01.91**

(71) Applicant(s)
DUBOIS CHEMICALS, INC.

(72) Inventor(s)
RONALD J. CHRISTENSEN; LYLE H. STEIMEL

(74) Attorney or Agent
SPRUSON & FERGUSON, GPO Box 3898, SYDNEY NSW 2001

(56) Prior Art Documents
US 4549968

(57) Claim

1. A method of removing dissolved oxygen from boiler feedwater, providing metal passivation and condensate treatment comprising:
 adding to said boiler feedwater an oxygen scavenging amount of a solution of ascorbic acid neutralized with diethylaminoethanol
 wherein said solution has a ratio of ascorbic acid to diethylaminoethanol of from 1/1 to about 1/15 on a molar basis; and
 wherein said solution has a pH of at least about 10; and
 maintaining said solution in said boiler to remove said dissolved oxygen and provide said passivation and condensate treatment.

605588

S & F Ref: 58345

FORM 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

COMPLETE SPECIFICATION

(ORIGINAL)

This document contains the
amendments made under
Section 49 and is correct for
printing

FOR OFFICE USE:

Class Int Class

Complete Specification Lodged:

Accepted:

Published:

Priority:

Related Art:

Name and Address
of Applicant:

DuBois Chemicals, Inc.
1100 DuBois Tower
Cincinnati Ohio 45202
UNITED STATES OF AMERICA

Address for Service:

Spruson & Ferguson, Patent Attorneys
Level 33 St Martins Tower, 31 Market Street
Sydney, New South Wales, 2000, Australia

Complete Specification for the invention entitled:

Oxygen Scavenger for Boiler Water and Method of Use

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

OXYGEN SCAVENGER FOR BOILER WATER AND METHOD OF USE

Background of the Invention

A recirculating boiler requires an extremely high purity of water in order to avoid a plurality of different problems. Unfortunately the quality of the water available for most boilers is such that the water employed would rapidly cause a deterioration of the boiler eventually requiring a shut down of the boiler and potential replacement of various portions of the boiler.

Currently there are a variety of different problems treated separately by a variety of different compositions. Two very major problems are scale formation and corrosion of the surface of the boiler. These two problems are interrelated in that corrosion of the surface is avoided by maintaining an alkaline pH. Scale formation is a problem which exists at alkaline pH's. Boilers generally operate under alkaline pH conditions and address the scale formation problem by the use of various scale inhibitors and descalants.

Even under alkaline conditions, there is a corrosion problem or pitting attributed to the presence of oxygen in the water. The key to solve this problem is to remove the oxygen. To avoid this problem, the make up water in a boiler is physically treated to deaerate the make up water. Oxygen scavenging chemicals are then added to further reduce the possibility of pitting. Chemicals commonly used for this purpose are sodium sulfite, catalyzed sodium sulfite, hydrazine and catalyzed hydrazine. Also, as disclosed in U.S. Patent No. 4,419,327 amine neutralized erythorbic acid can be used to scavenge oxygen. Ammonia is the preferred amine disclosed in this patent. Although other amines disclosed in this patent apparently have some catalytic affect on the erythorbic acid, this is not disclosed. Further the use of DEAE is not discussed in this patent. Ascorbic acid has also been discussed as an oxygen scavenger. It is structurally very similar to erythorbic acid, but has greater thermal stability.

Each of these have various problems. Sodium sulfite reacts with oxygen to form sodium sulfate. To scavenge oxygen effectively, eight parts of sodium sulfite are required for each part of dissolved oxygen. Sodium sulfite provides efficient scavenging in medium and low pressure boilers with no harmful by-products. Its use, however, is precluded in

boilers operating at or above 1800 psig where the high pressures cause the formation of SO_2 and H_2S by thermal decomposition of the chemical.

Hydrazine reacts with equal parts of oxygen to form inert nitrogen and water. Since the products are neutral, this treatment does not increase the dissolved solid concentrations in boiler water. Hydrazine is an effective scavenger at very low levels of application. Unfortunately, since it is volatile itself, it is susceptible to thermal decomposition to ammonium and nitrogen. The evolution of ammonium moreover may restrict hydrazine application to avoid corrosion.

In addition to oxygen pitting, there is a corrosion problem in the after boiler. Water invariably contains carbon dioxide and ammonia. The ammonia may be present in such trace levels that it is insufficient to either cause problems by overconcentration or to help combat the interaction of CO_2 with steam which forms carbonic acid in the condensate. Accordingly, volatile neutralizing amines such as cyclohexylamine, morpholine, diethanolamine and diethylaminoethanol are commonly used to combat corrosion in industrial after boiler sections by neutralizing condensate pH. These amines are present only for this purpose and do not have any reported oxygen scavenging affects.

SUMMARY OF THE INVENTION

The present invention is premised on the realization that an improved oxygen scavenging system can be formulated by combining ascorbic acid with a neutralizing amine and specifically diethylaminoethanol. The oxygen
5 scavenging effect of the ascorbic acid in combination with the diethylaminoethanol (DEAE) is greater than the oxygen scavenging effect of the ascorbic acid neutralized with sodium hydroxide. When added to boiling water in effective amounts, this composition provides both oxygen
10 scavenging and condensate treatment as well as metal passivation. In addition, the DEAE has an intermediate distribution ratio which provides condensate treatment for both long and short steam lines. This makes this combination particularly versatile.

The objects and advantages of the present invention will be further appreciated in light of the detailed description.

DETAILED DESCRIPTION

According to a first embodiment of the invention there is provided a method of removing dissolved oxygen from boiler feedwater, providing metal passivation and condensate treatment comprising:

adding to said boiler feedwater an oxygen scavenging amount of a
20 solution of ascorbic acid neutralized with diethylaminoethanol

wherein said solution has a ratio of ascorbic acid to diethylaminoethanol of from 1/1 to about 1/15 on a molar basis; and

wherein said solution has a pH of at least about 10; and
25 maintaining said solution in said boiler to remove said dissolved oxygen and provide said passivation and condensate treatment.

Ascorbic acid is combined with diethylaminoethanol to provide an oxygen scavenging solution which can be added in minor amounts to the make up water of a boiler to chemically scavenge oxygen. The combination of ascorbic acid and DEAE is formed by dissolving the ascorbic acid in water
30 and subsequently adding the DEAE to the ascorbic acid solution. As



purchased, the ascorbic acid is a 100% solid dry powder. Alternately, it can be in liquid form and can be neutralized sodium ascorbate.

The ratio by weight of ascorbic acid relative to DEAE can vary substantially and will range from about 1/1 to about 1/15 ascorbic acid to DEAE. The DEAE should be present in sufficient amount to adjust the pH of the ascorbic acid solution to at least about 7. Further, since the DEAE is also providing condensate treatment, it is preferable to add excess DEAE relative to the ascorbic acid raising the pH to at least about 7.5-8.5 in the condensate. Therefore the pH of the product (concentrate) should be about 11. The DEAE once added to the ascorbic acid solution is mixed thoroughly and provides a stable solution of ascorbate and diethylaminoethanol.

No further treatment of the solution is necessary. However, if the DEAE added does not increase the pH to about 10 added base may be needed to prevent bacterial growth.

The concentrated solution of ascorbic acid and DEAE should be from about 1% to 25% ascorbic acid and 1% to 50% DEAE. Basically, practicality sets the lower limit. A solution with an extremely low concentration will require that a large amount be added. This would be expensive because of shipping and storage costs.

Advantageously, this solution is compatible with many different components of a boiler water treatment system including sulfite, hydrazine, low molecular weight anionic polymers such as polymaleic anhydride, polymethacrylate, polyacrylate and phosphonates as well as soda ash and sodium glucoheptonate. Such a solution is disclosed in our pending application filed concurrently herewith entitled All-In-One Boiler Treatment Composition. These again would simply be added to the solution and mixed in.

The oxygen scavenging solution of the present invention is added to the boiler water at basically any point along the circulating water system of the boiler. Preferably, however, it is added to the deaerator storage sections.

Sufficient oxygen scavenging solution is added to establish or maintain the concentration of the oxygen scavenging solution within the boiler water at a desired and effective oxygen scavenging concentration. Basically, the concentration of the ascorbic acid in the solution must be from about 1 to about 40 parts per million with 10-20 ppm preferred. Ascorbic acid is consumed in use. Therefore the amount added is greater than the amount in the boiler. From about 1 to about 200 parts per million of DEAE should be present, preferably no more than 15 ppm in the steam.

In other applications, this may be increased. By maintaining this concentration, the present invention will provide both oxygen scavenging and condensate treatment.

The oxygen scavenging solution of the present invention is effective over a wide range of temperatures and pressure. Basically, the ascorbic acid and DEAE are effective up to about 1500 psi.

The present invention will be further appreciated in light of the following detailed example.

A 10 percent solution of ascorbic acid neutralized with DEAE to a pH of 9.8 was compared to NaOH neutralized ascorbic acid and hydrazine for oxygen scavenging capabilities in a 4 liter flask at room temperature. At 100 ppm the ascorbic acid/DEAE solution was 33% more effective than NaOH neutralized ascorbic acid and more than 100 times more effective than hydrazine under the same conditions.

The present invention provides oxygen scavenging and condensate treatment. Further, the condensate treatment, the DEAE, improves the efficiency of the oxygen scavengers.

The above has been a disclosure of the method of practicing the present invention as well as the best mode. However, the invention is defined by the following claims wherein we claim:

The claims defining the invention are as follows:

1. A method of removing dissolved oxygen from boiler feedwater, providing metal passivation and condensate treatment comprising:
adding to said boiler feedwater an oxygen scavenging amount of a solution of ascorbic acid neutralized with diethylaminoethanol
wherein said solution has a ratio of ascorbic acid to diethylaminoethanol of from 1/1 to about 1/15 on a molar basis; and
wherein said solution has a pH of at least about 10; and
maintaining said solution in said boiler to remove said dissolved oxygen and provide said passivation and condensate treatment.
2. The method claimed in claim 1 wherein said solution is added to the said feedwater in an amount sufficient to establish a concentration of at least 1 ppm ascorbic acid.
3. The method claimed in claim 2 wherein sufficient solution is added to establish a concentration of ascorbic acid of at least about 10 ppm.
4. The method claimed in any one of claims 1 to 3 wherein the concentration in said feedwater of diethylaminoethanol is established at least about 1 ppm.
5. A method of removing dissolved oxygen from boiler feedwater, substantially as hereinbefore described with reference to the detailed example.

DATED this SEVENTH day of JUNE 1990
DuBois Chemicals, Inc.

Patent Attorneys for the Applicant
SPRUSON & FERGUSON



_KEH/0078f