

16321/88

APPLICATION ACCEPTED AND AMENDMENTS

ALLOWED 13-7-90

FORM 1

601843

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;

Visual Analytical Tracer and Method for Detection and Quantitative Analysis for Water Treatment Chemicals

which is described in the accompanying complete specification.

Details of basic application(s):-

Basic Applic. No: Country:

131761

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 SEVENTEENTH day of MAY 1988

DuBois Chemicals, Inc.

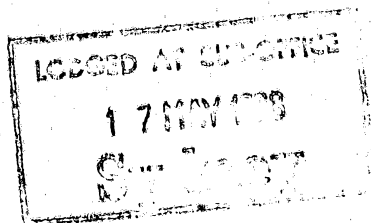
By:

M.J. Anderson

Registered Patent Attorney

TO: THE COMMISSIONER OF PATENTS
OUR REF: 58240
S&F CODE: 64180

5845/2



PATENT OFFICE



ONE HUNDRED DOLLARS

PATENT OFFICE



SIXTY DOLLARS

PATENT OFFICE



TEN DOLLARS

COMMONWEALTH OF AUSTRALIA
THE PATENTS ACT 1952
DECLARATION IN SUPPORT OF A
CONVENTION APPLICATION FOR A PATENT

AUSTRALIA
CONVENTION
STANDARD
& PETTY PATENT
DECLARATION
SFP 4

In support of the Convention Application made for a
patent for an invention entitled:

Title of Invention

VISUAL ANALYTICAL TRACER AND METHOD FOR DETECTION AND
QUANTITATIVE ANALYSIS FOR WATER TREATMENT CHEMICALS

I/We- I, Mark J. Hanket, Vice President
DuBois Chemicals, Inc.

Full name(s) and
address(es) of
Declarant(s)

of 1100 DuBois Tower
Cincinnati, Ohio 45202
United States of America

do solemnly and sincerely declare as follows:--

Full name(s) of
Applicant(s)

- ~~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
DuBois 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 the United States of America

Priority Date(s)

on December 11, 1987

Basic Applicant(s)

by Gary L. Baker and Ronald J. Christensen

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. Gary L. Baker Ronald J. Christensen
4368 S. Jerry Wright Rd. 8747 Tanager Woods Dr.
Alexandria, KY and Montgomery, Ohio
of both in 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

(12) PATENT ABRIDGMENT (11) Document No. AU-B-16321/88
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 601843

(54) Title
VISUAL ANALYTICAL TRACER AND METHOD FOR DETECTION AND QUANTITATIVE ANALYSIS FOR WATER TREATMENT CHEMICALS

International Patent Classification(s)
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(71) Applicant(s)
DUBOIS CHEMICALS, INC.

(72) Inventor(s)
GARY L. BAKER; RONALD J. CHRISTENSEN

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

(57) Claim

1. A method of detecting the concentration of a treatment composition present in the water in a water cooling tower comprising:
adding a mixture into said water, said mixture comprising a known amount of an inert photodegradable water soluble dye and a known amount of said treatment composition,
detecting the concentration of said treatment composition present in said water by photodetection of the concentration of said dye in said system.

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FORM 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

COMPLETE SPECIFICATION

(ORIGINAL)

FOR OFFICE USE:

Class Int Class

Complete Specification Lodged:
Accepted:
Published:

Priority:

Related Art:

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

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:

Visual Analytical Tracer and Method for Detection and
Quantitative Analysis for Water Treatment Chemicals

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

VISUAL ANALYTICAL TRACER AND METHOD FOR DETECTION
AND QUANTITATIVE ANALYSIS FOR WATER TREATMENT
CHEMICALS

Abstract of the Disclosure

An inert water soluble dye is added to a concentrated water treatment composition. This mixture is added to the water in a circulating water system such as a cooling tower. The concentration of the dye and the concentration of the actives in the treatment composition are proportionate to each other. The concentration of the treatment composition in the water system can be determined by measuring the percentage of light absorbed by the dye in the water. This can be determined by use of a colorimeter. Fluorescein is the preferred dye.

VISUAL ANALYTICAL TRACER AND METHOD FOR DETECTION
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CHEMICALS

Background of the Invention

There are many different types of circulating water systems. Three basic types are water cooling towers which are open systems, boilers which are closed systems, and chilled water systems which are also closed. More recently, cross-over cooling water systems, where both the tower water and the chilled water are combined for a period, are being employed.

If ultrahigh purity water were available in ample supply there would be little reason to chemically treat any of the water added to these systems. In actuality, however, highly pure water is rarely available. Therefore, operators of water systems must resort to chemical treatment to prevent damage to the water system which can be caused by the impurities contained in water.

There are literally dozens of treatment compositions that are currently added to these

systems. The selection of the particular treatment agent depends on the type of water added, the particular water system employed, and operational conditions. Some of the types of treatment compositions added include dispersants, descalants, scale inhibitors, algacides, biocides, corrosion inhibitors, oxygen scavengers and pH modifiers. In each category of composition there are also a number of different particular compositions which can be used to accomplish the desired result. For example, phosphonates are typically used as anti-scaling agents and corrosion inhibitors. Chelating agents such as ethylenediamine tetraacetic acid and nitrilotriacetic acid are also anti-scaling agents. Corrosion inhibitors also include aromatic azoles, alkaline earth metal molybdates and so on.

Water systems are treated by adding the selected desired treatment agents separately or more likely a combination of treatment agents is dispensed into the water in the water system. Combinations for example could include corrosion inhibitors in combination with descalants and biocides for a water cooling tower. A boiler treatment composition may for example include an anti-scalant, corrosion inhibitors and oxygen scavenger.

Whether the treatment compositions are added separately or as a mixture it is necessary to

determine the concentration level of the treatment agent or agents in the water system. Typically this has been done by simply taking a sample of the water in the system and performing a series of chemical analysis such as pH and various titrations to determine the concentration of the chemicals added.

One chemical that has been added in the past has been tannins and a similar composition lignins. These are anionic compositions which have been used in the past as dispersants. They are no longer the preferred dispersants since certain water soluble polymers have been developed which by far surpass the dispersing activities of these chemicals. However, these chemicals did have one incidental advantage in that they had a color and could be visually detected within a water system. Thus the boiler operator could visually detect the concentration of tannin or lignin in the system. When used they were added separately to the system. Therefore they did not provide any indication of the concentration of any other component.

Because tannins and lignins are anionic they cannot be added to a mixture which includes cationic treatment agents such as other dispersants and the like which can be cationic. In concentrated solutions, the tannins and lignins would precipitate out of solution and be totally ineffective.

Accordingly, to determine the concentration of the treatment agents in a water system one must perform complex titrations and other tests. This is inefficient and can result in ineffective treatment or a waste of treatment agents.

Summary of the Invention

The present invention is premised on the realization that a inert water soluble dye can be added and mixed with a concentrated treatment agent for a water system and be dispensed into the water system with the treatment agent. Since the amount of dye added to the water system is proportional to the amount of treatment agent added, the concentration of the treatment agent can be determined by measuring the concentration of the dye. Thus, the intensity of the color of the water provides an indication of the concentration of the treatment agent.

The present invention is further premised on the realization that the concentration of the treatment agent can then be detected by photometric and/or visual means and more specifically by a colorimetric method using visible light detectors. Fluorometric techniques may also be used. Selecting a dye with an absorbance which varies linearly with concentration at application concentration simplifies colorimetric analysis.

A photodegradable dye can be employed which when dispensed into the environment does not have a long lasting and noticeable effect on the environment and thus is environmentally acceptable. Surprisingly even in open systems such as water cooling towers where the water treatment agent is exposed to sunlight for a period of time a photodegradable dye can be employed without being totally inactivated when exposed to the light.

The advantages of the present invention will be further appreciated in light of the following detailed description and drawing in which:

Brief Description of the Drawing

The figure is a graphical depiction of the percent transmittance of 500nm light relative to the concentration of a fluorescein dye.

Detailed Description of the Invention

The present invention is a method of detecting the concentration of a water treatment composition in a water circulating system. The water treatment composition is a water based concentrated composition which incorporates a known quantity of a water soluble dye as well as a known quantity of one or more water treating chemicals. By detecting the concentration of the dye in a circulating water system one can also detect the corresponding concentration of the active ingredients of the water treatment

composition or determine the amount of treatment product added. Also, when slug doses of the treatment is initially added, system water volume can be determined.

Accordingly, this invention provides a method of detecting the
5 concentration of a treatment composition present in the water in a water cooling tower comprising:

adding a mixture into the water, the mixture comprising a known amount of an inert photodegradable water soluble dye and a known amount of the treatment composition,

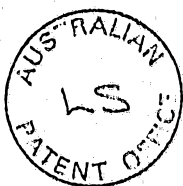
10 detecting the concentration of the treatment composition present in the water by photodetection of the concentration of the dye in the system.

For the purposes of the present invention, a water circulating system also includes evaporative condensers, boilers, and chilled water systems.

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Each of these systems require one or more treating chemicals or agents added to the water in the systems. Treatment compositions for the present invention basically includes any chemical which will be added to the water of a water cooling tower, boiler or chilled water system to alter any physical or chemical activity of the water. These chemical compositions include dispersants including organophosphorous compounds particularly organophosphorous carboxylic acids and the phosphonates. Typically the phosphonates include aminomethylene phosphonic acid and 1-hydroxyethyladene-1,1-diphosphonic acid. A commonly employed organic phosphorus carboxylic acid is 2-phosphonobutane-1,2,4-tricarboxylic acid.

25 These chemical compositions also include corrosion inhibitors such as alkaline earth metal molybdates, chromates and nitrite salts which are used at higher concentrations. Sodium molybdate is an anodic inhibitor and is the most commonly used



molybdate inhibitor. Other corrosion inhibitors include aromatic azoles primarily used as corrosion inhibitors for copper and its alloys. Generally included within the aromatic azoles are benzotriazole, tolyltriazole and mercaptobenzothiazole.

Biocides are also employed. These may include ClO_2 , chlorine, chlorine release compounds such as chlorinated isocyanurates, hypochlorites, and chlorinated hydantoins. Oxidizers such as chlorine, present in the cooling water system at concentrations greater than about 0.5 ppm, will degrade the fluorescein. Hydrogen peroxide tends to cause precipitation of the fluorescein when added to the treated cooling water. Quaternary ammonium compounds are the primarily non-oxidizing biocides and biostats. These are cationic surface active chemicals which are most effective against algae and bacteria at alkaline pH.

Chelants are also used as hardness sequestering agents. These include ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA).

Anionic polymers are widely used in industrial boilers for sludge conditioning. These are credited with inhibiting scale formation and with removing existing scale by several mechanisms. Such anionic polymers include polyacrylates, polymethacrylates, polymaleic anhydride and various copolymers

of these. Synthetic sulfonated polymers, synthetic carboxylated polymers and carboxymethylcellulose are also used.

Oxygen scavengers are used primarily in boiler operations and chilled water systems. Oxygen scavengers include sodium sulfite, hydrazine and erythorbic acid and salts thereof. In boilers neutralizing amines are used to combat the interaction of carbon dioxide with steam which forms carbonic acid. The neutralizing amines may include cyclohexylamine, morpholine, and diethylaminoethanol. Filming amines are used to establish a continuous protective film over surfaces in the after boiler section. These would include octadecylamine.

There are also a variety of different chemicals used to adjust boiler water pH including sodium hydroxide and sodium carbonate. Other compositions may include sodium nitrate which inhibits caustic embrittlement, and anti-foaming agents like polyglycols, silicones and polyamides.

One or more of these chemical compositions or agents are added to a water system in an attempt to attain a desired use concentration generally defined in parts per million of the actives of the chemical compositions. These are however purchased and dispensed as concentrated aqueous solutions which are generally defined in terms of grams of actives per

liter of concentrated treatment composition. Where the treatment composition is a mixture of treatment agents the concentration of each agent is proportioned to the desired use concentration.

Thus a known concentration Q_1 of an inert water soluble dye is added to the concentrated treatment composition. For use in the present invention the water soluble dye must be inert. For purposes of the present invention, inert means that it must have neither appreciable anionic nor cationic characteristics in concentrated forms. It must also be thermally stable, and stable to both reducing and slightly oxidizing environments.

The dye must be photodetectable to provide advantageous benefits of the present invention. By photodetectable it must be detected by light reflectance, transmittance or absorbance in the ultraviolet, infrared, or visible spectrums. Preferably, the dye will be fluorescent and detectable by one of these means using visible light. Under these circumstances the concentration can be initially visually detected and can subsequently be detected by means of a colorimeter which is quite inexpensive relative to ultraviolet and infrared spectrophotometers. Visual detection can be facilitated by the use of a color comparator.

Further, since most water systems periodically bleed off water in the system and dispense this into the environment, the dye should be nonstaining and non-persistent. More particularly it should be a dye which degrades naturally and quickly in the environment and preferably would be a photodegradable dye. Suitable non-persistent dyes include fluorescein, Rhodamine B, Rhodamine WT and Lissamine. All of these are non-persistent and are currently used in water flow studies in the environment. A preferred dye is fluorescein which degrades very quickly in the environment.

The dye will be added to the concentrated treatment composition and dispensed with the treatment composition into the water system. The amount of dye added to the concentrated treatment composition will depend on the amount of treatment composition intended to be added to the water system to provide the desired concentration level of the treatment composition generally in terms of parts per million. It is preferable that the concentration of the dye present in the water system will be within a concentration range where the change in amount of dye will provide a linear response on the spectrophotometer. This is shown with respect to fluorescein in the figure.

This figure shows the percent transmittance of light at 500nm versus the concentration of

fluorescein at a concentration level of 0.3-3 parts per million. At this concentration range the change in concentration of fluorescein with respect to transmittance is basically linear making it very easy to determine photometrically the concentration of fluorescein in the water system.

Since the concentration of the fluorescein in the treatment agent is known and the concentration of the fluorescein in the water can be detected, the concentration of the water treatment agent can be determined. The optimum concentration of fluorescein is 1.2 ppm. Thus, where the desired concentration of treatment composition is 120 ppm, the treatment composition should be 1% fluorescein.

This of course will change depending on the dye used, the wave length of light at which this is measured and the optimum concentration of the particular dye.

The invention will be further appreciated in light of the following examples of concentrations of components that could be added to boilers, water cooling towers and chilled water systems. These provide typical desired optimum concentrations and typical desired concentrations of the fluorescein dye that would be added to these compositions.

Cooling Water Treatment Formula

<u>Order of Addition</u>	<u>Ingredient</u>	<u>Percent</u>
1	Water	87.6
2	Phosphonate (HEDP - 60%)	3.0
3	Polyacrylic Acid - 50%	1.0
5	Tolyltriazole - 50%	2.0
6	Fluorescein	0.4
4	Sodium Hydroxide - 50%	6.0

Applied at 300-600 ppm conc. in the system.

Boiler Water Treatment Formula

<u>Ingredient</u>	<u>Percent</u>
Water	72.35
Disodium Phosphate	6.00
Polyacrylic Acid - 50%	1.50
Sodium Sulfite	5.00
Potassium Hydroxide	15.00
Fluorescein	0.15

Maintained at 800 to 1200 ppm in the boiler.

These compositions are added merely by way of example and the particular chemical compositions that would be added or combinations of chemical compositions that would be added to the particular system will vary widely particularly depending on the make-up water added to the system which varies based on geographic location.

In carefully conducted field tests where a water treatment composition having .4% fluorescein was added to a water cooling tower, the accuracy of this method was compared to a standard industry test, the thorium nitrate test. By measuring make up water and the mass of treatment composition added, the concentration was determined to be 384 ppm. Using a color-

imeter to detect the concentration of fluorescein, the concentration was measured at 341 ppm. Using color comparator, the concentration was determined to be 400 ppm. The thorium nitrate test, which tests for phosphonate concentration, indicated the concentration was 469 ppm. Thus, detecting concentration by detecting fluorescein concentration is substantially more accurate than the thorium nitrate test and much simpler to apply.

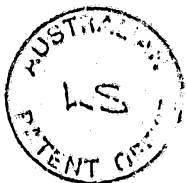
The proceeding has been a detailed description of the present invention. This has been exemplary in nature and is intended to describe how to practice the invention as well as the best mode of practicing the invention. However, as is obvious from the specification this can be modified by various changes in treatment compositions, dyes and detection techniques. Thus, the present invention should be limited only by the following claims in which we claim:

The claims defining the invention are as follows:

1. A method of detecting the concentration of a treatment composition present in the water in a water cooling tower comprising:
adding a mixture into said water, said mixture comprising a known amount of an inert photodegradable water soluble dye and a known amount of said treatment composition,
detecting the concentration of said treatment composition present in said water by photodetection of the concentration of said dye in said system.
2. The method according to claim 1 wherein said dye is selected from the group consisting of fluorescein, Rhodamine B, Rhodamine WT and Lissamine.
3. The method according to claim 2 wherein the dye is fluorescein.
4. The method according to claim 3 wherein said fluorescein is maintained at concentration levels between 0.3 and 3.0 ppm.
5. The method according to any one of claims 1 to 4 wherein the concentration of said dye is visually detected.
6. A method of detecting the concentration of a treatment composition present in the water in a water cooling tower substantially as hereinbefore described with reference to any one of the Examples.

DATED this FIFTH day of JULY 1990
DuBois Chemicals, Inc.

Patent Attorneys for the Applicant
SPRUSON & FERGUSON



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