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2 CORROSION INHIBITION IN HIGH TEMPERATURE ENVIRONMENT
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4 Field of Invention

5 This invention pertains to high temperature corrosion, and
6 more particularly, to the inhibition of high temperature corrosion
7 with tin oxide.
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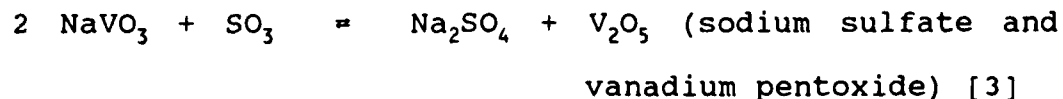
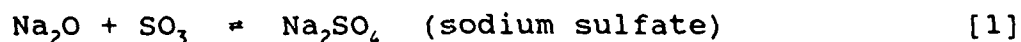
9 Background of Invention

10 Many low cost, low grade petroleum and coal fuels contain
11 appreciable levels of sodium, sulfur, and vanadium. Low quality
12 marine residual fuels, for example, may contain up to 0.2 weight
13 percent ash which contains appreciable amounts of sodium, up to 5
14 weight percent sulfur and up to 0.06 weight percent or 600 ppm
15 vanadium. Low grades of marine distillate fuels are allowed up to
16 0.05 weight percent ash which contains appreciable amounts of
17 sodium, up to 2 weight percent sulfur and up to 100 ppm vanadium.
18 In addition, salts containing sodium, sulfur, and vanadium may also
19 be ingested in the air intake of an engine or furnace operating in
20 dusty or sea mist laden environments. Waste materials being burned
21 in incinerators may, likewise, contain sodium, sulfur and vanadium.

22 In high temperature, oxygen-rich combustion environments,
23 sodium, sulfur and vanadium are oxidized predominantly to the
24 oxides of sodium, sulfur and vanadium, particularly sodium oxide,
25 sulfur trioxide and vanadium pentoxide. These oxide species
26 interact and condense as corrosive, molten deposits on such

1 components as gas turbine blades, diesel engine exhaust valves and
2 pistons, boiler tubes, and incinerator walls, or if gaseous, are
3 found in the gas phase above. The corrosion caused by such
4 deposits can be virulent and highly damaging, with the service life
5 of the component being reduced by 80% or more, in some instances.

6 Molten deposits of this type are commonly described as "sodium
7 sulfate-sodium vanadate" or "sulfate-vanadate" deposits. They
8 contain sodium oxide, sulfur trioxide, sodium sulfate, sodium
9 vanadate, and possibly other components, with sulfur trioxide gas
10 in the gaseous phase above the deposits. Concentrations of the
11 individual components in the molten and gaseous phases are fixed by
12 such simultaneous chemical reactions as:



18
19 The concentrations of the different components in the molten
20 deposits and the gaseous phase thereabove depend also on the Na/V/S
21 ratios in the fuel and intake air, as well as the temperature.
22 Note that by reaction [3], an increase in the fuel sulfur content,
23 for a fixed Na/V ratio, increases not only the Na_2SO_4 concentration
24 but also the V_2O_5 concentration in the molten deposit.

25 Molten salt corrosion, or "hot corrosion", results when the

1 oxides of sodium, sulfur and vanadium, such as Na_2O , SO_3 , and V_2O_5 ,
2 react with the protective surface oxide layer that exists on high
3 temperature substrates, particularly metal alloys or ceramics.
4 Under various circumstances, reaction with either sodium oxide,
5 sulfur trioxide or vanadium pentoxide may be the predominant cause
6 of hot corrosion. For example, in the well known "basic fluxing"
7 mode of hot corrosion at 900°C , Na_2O from Na_2SO_4 -rich deposits reacts
8 with the alumina surface film on gas turbine superalloys to form
9 nonprotective NaAlO_2 which causes catastrophic hot corrosion. High
10 temperature chromium-containing metals which rely on chromia
11 protective surface oxide are also corroded by Na_2SO_4 -rich deposits
12 via formation of nonprotective Na_2CrO_4 . Conversely, in 700°C "low
13 temperature" hot corrosion, sulfur trioxide gas, which is present
14 in the corrosive environment, reacts with cobalt oxide from
15 CoCrAlY turbine blade coatings to form low-melting mixed CoSO_4 -
16 Na_2SO_4 eutectic deposits and yields an "acidic fluxing" type of hot
17 corrosion. Fuels containing vanadium often cause a "vanadate" type
18 of hot corrosion wherein vanadium pentoxide from the molten deposit
19 reacts with nickel oxide or cobalt oxide from nickel-based or
20 cobalt-based superalloys, or with ferric oxide from high
21 temperature steels, to produce spalling metal vanadates.

22 Similar hot corrosion reactions involving sodium oxide, sulfur
23 trioxide, and vanadium pentoxide occur with ceramics. For
24 instance, sodium oxide from Na_2SO_4 -rich molten deposits reacts with
25 the surface film of silica that normally protects silicon carbide

1 and silicon nitride ceramics in oxygen-rich engine environments.
2 This type of hot corrosion represents a serious threat to the use
3 of silicon carbide and silicon nitride components in land and
4 marine engines. High sulfur fuels, containing in excess of 1
5 weight percent sulfur, attack yttria-stabilized zirconia thermal
6 barrier coatings through reaction of the engine gas sulfur trioxide
7 with yttria to form low-melting eutectic sulfate mixtures. The
8 reaction of yttria in yttria-stabilized zirconia with the vanadium
9 pentoxide component of sulfate-vanadate engine deposits is another
10 ceramic hot corrosion problem which, at present, precludes use of
11 yttria-stabilized zirconia thermal barrier coatings in marine and
12 land engines burning fuels which contain vanadium.

13 Therefore, no material is known which inhibits hot corrosion
14 in the presence of vanadate-sulfate molten deposits containing high
15 concentrations of oxides of sodium and vanadium in the melt and
16 gaseous oxides of sulfur in the gaseous phase thereabove.

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Summary of Invention

19 An object of this invention is the inhibition of corrosion in
20 a hot atmosphere containing corrosive components by the use of an
21 inexpensive material which is nonreactive with the corrosive
22 components.

23 Another object of this invention is the inhibition of hot
24 corrosion by the use of a tin oxide.

25 These and other objects of this invention are accomplished by

1 combusting a fuel containing sodium, vanadium and sulfur to form
2 reaction products containing oxides of sodium, vanadium and sulfur,
3 and contacting a structural member with the reaction products, the
4 structural member comprising tin oxide.

5
6 Detailed Description of the Invention

7 The invention described and claimed herein pertains to a
8 method which comprises the step of contacting a structural member
9 with oxides of sodium and sulfur at a temperature exceeding 300°C,
10 the structural member comprising tin oxide.

11 More specifically, this invention pertains to a method for
12 combusting a hydrocarbon fuel in an engine, a furnace, an
13 incinerator or another high temperature apparatus. The hydrocarbon
14 fuel contains sodium, sulfur and vanadium and forms, on combustion,
15 reaction products containing oxides of sodium, sulfur and vanadium.
16 In order to inhibit corrosion in a hot atmosphere, the method also
17 includes the step of contacting the reaction products with a
18 structural member comprising tin dioxide at a temperature of 300-
19 1500°C, preferably 500-1000°C.

20 Although combustion temperature of a hydrocarbon fuel is well
21 above 2000°C, it is believed that contact between the gaseous
22 reaction products and the structural members takes place at a
23 temperature in the approximate range of 300-1500°C, preferably 500-
24 1000°C. At these temperatures, in an atmosphere containing
25 sufficient oxygen, it is believed that sodium, sulfur and vanadium

1 exist as oxides, including sodium oxide, sulfur trioxide and
2 vanadium pentoxide.

3 To be useful as an inhibitor in a hot corrosion environment as
4 herein described, tin oxide, particularly tin dioxide, must meet
5 certain physical as well as chemical requirements. The oxide must
6 have the structural strength, thermal shock tolerance, erosion
7 resistance, etc., to make it capable of being used as a coating or
8 cladding, or of being fabricated into objects or components for use
9 in engines or other high temperature applications. It must have
10 sufficiently low volatility to be able to survive for long periods
11 at high temperature, and finally, the oxide must be stable, i.e.,
12 not reducible, at the oxygen partial pressures existing in the
13 given high temperature environment.

14 Tin dioxide has a melting point of 1630°C. It has good
15 thermal shock resistance and is potentially useable at temperatures
16 of up to 1500°C in oxidizing environments. Tin dioxide has a Knoop
17 hardness of about 1000 to 1600 kg mm⁻², varying because of
18 anisotropy, and thus should have an erosion resistance falling
19 between that of ZrO₂, which has a hardness of 1160 kg mm⁻², and
20 Al₂O₃, which has a hardness of 2000 kg mm⁻², since the erosion
21 resistance of oxides is principally a function of hardness. The
22 vapor pressure of tin dioxide is higher than that of most
23 refractory ceramic oxides, having maximum evaporation rates of
24 about 1×10^{-15} g/cm²-sec at 1100K (827°C) and 1×10^{-9} g/cm²-sec at
25 1300K (1027°C), under 0.2 bar of oxygen. However, the loss of tin

1 oxide by evaporation from components in engines or furnaces at
2 operating temperatures should be negligible. For instance, even at
3 1300K (1027⁰C), the evaporation rate corresponds to a loss of less
4 than 0.0002 inches per year from a solid tin dioxide surface.

5 Although tin dioxide is more easily reduced than alumina or
6 zirconia, it is in fact more resistant to reduction than nickel
7 oxide and ferric oxide, both of which are found as stable oxides in
8 engines and other high temperature environments. Tin dioxide,
9 therefore, has physical properties which make it suitable for use
10 as a corrosion-resistant material in engines and other applications
11 having oxidizing environments and high temperatures.

12 Tin dioxide does not react with the oxides of sodium, sulfur,
13 and vanadium at temperatures below about 1500°C in an oxygen-
14 containing atmosphere. More specifically, tin dioxide does not
15 react with vanadate-sulfate deposits at 700°C or at 800°C under
16 sulfur trioxide partial pressure of from about 1×10^{-7} bar to about
17 1×10^{-2} bar. Indeed, it is believed that tin dioxide will give
18 improved corrosion resistance even beyond these ranges.

19 The structural member that comes in contact with the reaction
20 products can be made from tin dioxide itself or tin dioxide in
21 admixture with other materials. Since tin dioxide is a white
22 powder at room temperature, the structural member of tin dioxide or
23 the mixtures may be made by pressing and sintering of tin dioxide
24 or the mixtures in the form of the structural member.

25 The structural member which contacts the reaction products can

1 also be made of a substrate and at least one coating thereon. The
2 substrate and the at least one coating thereon are designed to
3 withstand the high operating temperatures.

4 The substrate can be made of a metal, such as the metallic
5 superalloy Rene 80, or a ceramic, such as silicon nitride or
6 silicon carbide. Rene 80 is a nickel-based superalloy used for gas
7 turbine blades. Specific examples of structural members composed of
8 a substrate and at least one coating thereon include marine and
9 industrial gas turbine blades, which are expected to withstand
10 temperatures of about 700° to 900°C, and diesel engine exhaust
11 valves and pistons, which are expected to withstand temperatures of
12 about 500°C to 800°C.

13 The thickness of the substrate can vary widely. For instance,
14 pistons in some ship diesel engines can be about four feet in
15 diameter and the exhaust valves can be over one foot in diameter.
16 The thickness in these parts can vary widely from about 1/16 of an
17 inch to several inches, such as about 5 inches, preferably 1/2 of
18 an inch to 3 inches. In jet engines, the thickness of the substrate
19 is generally in the range of 0.05-10 millimeters, but more commonly
20 1-5 millimeters. The thickness of the substrate is not considered
21 to be critical in this invention.

22 Various coatings are commonly provided on the substrate to
23 function as a thermal barrier, to protect from wear or as an
24 inhibitor to reduce high temperature corrosion. An example of
25 thermal barrier coatings is stabilized zirconia, an example of a

1 wear coat is zirconia infiltrated with chromia and examples of high
2 temperature corrosion-resistant coatings are alloys of cobalt or
3 nickel containing chromium, aluminum, and yttrium. Presence of
4 yttrium in the corrosion resistant coatings is optional. Further
5 examples of high temperature corrosion-resistant coatings are the
6 "aluminides" and "silicides", which are produced by diffusing
7 aluminum and silicon, respectively, into the surface of superalloys
8 or other substrates. Other metallic or ceramic coatings can also
9 be used.

10 Tin dioxide itself can be applied as an outer coating directly
11 on the substrate, on another coating as an outer coating, or it can
12 be applied as a component of an outer coating in order to further
13 inhibit high temperature corrosion caused by molten oxides of
14 sodium and vanadium in the sodium-vanadate melt and gaseous oxide
15 of sulfur in the vapor phase. When tin dioxide is applied as the
16 principal ingredient onto a substrate as a coating, a portion of
17 the coating may consist of other materials. The amount of tin
18 dioxide in such coatings can vary from 50 -100% by weight. When tin
19 dioxide is applied as a component of another coating where it is
20 not the principal ingredient, amount thereof in the coating can be
21 1-50%, preferably 5-30% by weight.

22 The thickness of the coating which contains tin dioxide or
23 which is composed solely of tin dioxide are typically from about
24 0.5 to about 500 microns, preferably 2-250 microns. Thicker
25 coatings provide greater protection but are likely to be more prone

1 to spalling. However, thick thermal barrier coatings are also known
2 which have thickness of up to about 0.5 of an inch, especially from
3 about 0.05 up to about 0.25 of an inch. Pursuant to this invention,
4 such coatings would also comprise tin dioxide.

5 An important application of the present invention is the use
6 of tin dioxide as a stabilizer for zirconia thermal barrier
7 coatings to produce zirconia stabilized with tin dioxide having
8 superior resistance to molten vanadate-sulfate hot corrosion in
9 presence of sulfur trioxide gas. Tin dioxide stabilizes zirconia
10 in its high temperature tetragonal or cubic structures. Such
11 stabilization avoids the catastrophic monoclinic-to-tetragonal or
12 cubic transformation of zirconia that normally occurs with thermal
13 cycling and so allows the use of stabilized zirconia in engines.
14 When stabilized with tin dioxide, zirconia can form solid solutions
15 with tin dioxide. The amount of tin dioxide in stabilized zirconia
16 compositions or other anti-corrosion coating compositions is
17 typically 1-50%, preferably 5-30% by weight.

18 Numerous methods exist which can be used to deposit tin oxide
19 coatings on substrates, on other coatings or as a component part of
20 a coating. These include spray pyrolysis, slurry coating, electron
21 beam physical vapor deposition, chemical vapor deposition, sputter
22 coating, and others. In reference specifically to the stabilized
23 zirconia coatings, the tin dioxide stabilized zirconia coatings can
24 be applied by electron beam physical vapor deposition or by plasma
25 spraying of tin dioxide and zirconia powders.

1 Since tin has a melting temperature of 232°C, it would not be
2 structurally useful at temperatures above its melting point.
3 However, tin can be alloyed with other metals and may produce a tin
4 oxide-containing coating which could be resistant to high
5 temperature corrosion by sulfate-vanadate melts in presence of
6 sulfur trioxide gas. The term "tin oxide" as used herein, includes
7 general forms of oxides of tin such as tin monoxide and tin
8 dioxide.

9 The invention having been generally described, the following
10 examples are given as particular embodiments of the invention to
11 demonstrate the practice and advantages thereof. It is understood
12 that the examples are given by way of illustration and are not
13 intended to limit the specification or the claims that follow, in
14 any manner.

15
16 Example 1

17 This example demonstrates that tin dioxide is highly resistant
18 to high temperature reactions with sodium oxide (Na_2O) and vanadium
19 pentoxide (V_2O_5) over a wide range of sodium oxide and vanadium
20 pentoxide concentrations.

21 Equimolar mixtures of tin dioxide with each of the vanadium-
22 containing compounds V_2O_5 , $\text{Na}_2\text{V}_{12}\text{O}_{31}$ ($\text{Na}_2\text{O} \cdot 6\text{V}_2\text{O}_5$), NaV_3O_8 ($\text{Na}_2\text{O} \cdot 3\text{V}_2\text{O}_5$),
23 NaVO_3 ($\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_5$), and Na_3VO_4 ($3\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_5$) were thoroughly ground and
24 mixed together, and then heated in platinum boats over a period of
25 20-24 hours at 680°C in one test and at 800°C in a second test.

1 At the end of the heating periods, the mixtures were removed
2 from the furnace and platinum boats, and subjected to x-ray
3 diffraction analyses for evidence of reaction. In each case, there
4 was no evidence of products being formed or any other indication of
5 reaction. The tin dioxide x-ray diffraction pattern remained
6 unchanged in terms of both absolute and relative peak intensities
7 as well as interplanar distances. This confirms that tin dioxide
8 was not consumed to form an amorphous product or any other product.
9 Also, the fact that the relative peak intensities were not changed
10 is evidence that tin dioxide was not dissolving in the melts and
11 then precipitating upon cooling, since precipitated crystallites
12 develop preferred growth habits that would have caused large and
13 readily detectable changes in the relative intensities of the x-ray
14 peaks.

15 This example is important for another reason: whereas a
16 technical article alleges that tin dioxide reacts with vanadium
17 pentoxide, this example shows that tin dioxide does not react with
18 vanadium pentoxide at the temperature involved.

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Example 2

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In this example, thermogravimetric analysis procedure was used
to determine if tin dioxide (SnO_2) reacted with sodium oxide (Na_2O)
or vanadium pentoxide (V_2O_5) components of vanadate-sulfate molten
deposits in the presence of sulfur trioxide (SO_3) gas. The
vanadate-sulfate deposits were produced by reacting sodium vanadate

1 (NaVO₃) with sulfur trioxide at different partial pressures of
2 sulfur trioxide yielding deposits which were mixtures of sodium
3 vanadate (NaVO₃), sodium sulfate (Na₂SO₄) and vanadium pentoxide
4 (V₂O₅), where sodium sulfate and vanadium pentoxide concentrations
5 increased with increasing partial pressure of sodium trioxide. The
6 tests were conducted at 700°C and at 800°C, at which temperatures
7 the deposits were molten.

8 Pursuant to the procedure herein, the thermobalance, furnace,
9 and gas handling systems used are described and illustrated in the
10 article by R.L. Jones, the inventor herein, entitled
11 "Thermogravimetric Study of the 800°C Reaction Zirconia Stabilizing
12 Oxides with SO₃-NaVO₃", in Journal of Electrochemical Society,
13 139[10], pp. 2794-2799 (1992), except that the exit passageway of
14 the balance counterflow air has been slightly modified to prevent
15 SO₃ condensation on the balance hangwire at high SO₃ concentrations.
16 The test temperatures of 700 and 800°C were chosen both as being
17 suitable for the experimental procedure and as being temperatures
18 at which SnO₂ might ultimately be used. The test specimens
19 consisted of 0.41 mmol (50 mg) of dry NaVO₃ and 0.41 mmol (50 mg)
20 of dry NaVO₃ mixed with 0.10 mmol (15 mg) SnO₂. The specimens were
21 held in the atmosphere for in excess of 24 hours where partial
22 pressure of SO₃ was varied from about 1 x 10⁻⁷ bar to about 1 x 10⁻³
23 bar.

24 By weight gain analysis and x-ray diffraction analysis, it was
25 shown that tin dioxide reacted with neither pure sodium

1 metavanadate (NaVO_3) nor with the vanadate-sulfate deposit systems
2 in the presence of sulfur trioxide at 700°C nor at 800°C . At
3 700°C , the calculated approximate deposit compositions, in mole
4 percent, at the indicated sulfur trioxide partial pressures were as
5 follows:

	<u>1×10^{-7} bar</u>	<u>1×10^{-3} bar</u>
6 NaVO_3	76%	14%
7 Na_2SO_4	12%	43%
8 V_2O_5	12%	43%

10 At 800°C , the calculated approximate deposit compositions, in mol
11 percent, at the indicated sulfur trioxide partial pressures were as
12 follows:

	<u>1×10^{-7} bar</u>	<u>1×10^{-3} bar</u>
13 NaVO_3	85%	26%
14 Na_2SO_4	7.5%	37%
15 V_2O_5	7.5%	37%

17 In this example, NaVO_3 was considered to simulate an engine
18 deposit having Na/V ratio of 1 that exists in equilibrium with the
19 SO_3 in the combustion gas. The equilibrium is described by the
20 reaction:



22 Published thermodynamic calculations indicate that this equilibrium
23 reaction should be predominant under gas turbine conditions.

24

25 Example 3

26 This example demonstrates preparation of zirconia stabilized
27 with tin dioxide.

28 After tin chloride (SnCl_4) of commercial grade purity is

1 dissolved in cold water, this solution is added to an appropriate
2 quantity of zirconium oxychloride ($ZrOCl_2$) dissolved in 3 molar
3 hydrochloric acid.

4 The acid solution is neutralized with a stoichiometric excess
5 amount of 3 molar ammonium hydroxide. The precipitate, which forms
6 on neutralization, is collected by filtration, washed several times
7 with deionized water and dried. The precipitate is calcined for
8 1/2 hour at $600^\circ C$ to drive off all traces of ammonium chloride.

9 Pellets are formed of the precipitate by pressing the material
10 in a uniaxial die system at 4000 psi. The pellets thus formed are
11 then isostatically pressed at 25,000 psi to obtain a dense ceramic
12 structure. This dense pellet is fired at $1300^\circ C$ for 3 hours
13 whereby a solid solution is believed to be formed of zirconia and
14 tin dioxide and the tetragonal or cubic crystal structure is
15 produced.

16 The zirconia stabilized with tin dioxide formed as described
17 in this example can be ground and applied in known manner, as by
18 means of plasma spray, to a substrate in need of protection from
19 high temperature corrosion.

20 In some circumstances, a binder or a bond coat may be
21 necessary between the substrate and the stabilized zirconia
22 coating. Any of the known binders or bond coats for zirconia
23 coatings may be used for this purpose.

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Docket No.: NC 75,053
Inventor's Name: Jones, R.L.

Patent Application

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Abstract of Disclosure

This invention pertains to the use of tin oxide as a corrosion resistant material for preventing or inhibiting high temperature corrosion by molten sulfate-vanadate deposits and gaseous sulfur trioxide formed in engines or other high temperature apparatus which burn materials containing sodium, sulfur, and vanadium.

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