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(54) Title: METHOD FOR PREPARING AND USING SILICATE SYSTEMS TO TREAT ELECTRICALLY CONDUCTIVE SURFACES AND PRODUCTS OBTAINED THEREFROM

(57) Abstract: The disclosure relates to treating a silicate medium and using the treated medium for improving the surface of metallic or electrically conductive materials. The treated medium provides a silicate medium having a defined degree of polymerization and predetermined quantities of the desired silicate polymer. The treated silicate medium can be employed in an electroless or electrolytic process.



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5 **METHOD FOR PREPARING AND USING SILICATE SYSTEMS TO TREAT
ELECTRICALLY CONDUCTIVE SURFACES AND PRODUCTS OBTAINED
THEREFROM**

10 **[0001]** This application claims the benefit of U.S. Provisional Application No. 60/465,414,
filed April 25, 2003, U.S. Provisional Application No. 60/510,230, filed on October 08, 2003
and U.S. Provisional Application No. 60/528,034, filed on December 09, 2003. The disclosure
of the previously identified Provisional Applications is hereby incorporated by reference.

15 **FIELD OF THE INVENTION**

[0002] The instant invention relates to preparing silicate mediums and using silicate
mediums for modifying the surface of metals and other electrically conductive materials.

BACKGROUND OF THE INVENTION

20 **[0003]** Silicates have been used in electrocleaning operations to clean steel, tin, among other
surfaces. Electrocleaning is typically employed as a cleaning step prior to an electroplating
operation. Usage of silicates for cleaning described in "Silicates As Cleaners In The Production
of Tinplate" is described by L.J. Brown in February 1966 edition of Plating; European Patent
No. 00536832/EP B1 (Metallgesellschaft AG); and U.S. Patent Nos. 5,902,415, 5,352,296 and
25 4,492,616.

[0004] Processes for electrolytically forming a protective layer or film by using an anodic
method are disclosed by U.S. Patent No. 3,658,662 (Casson, Jr. et al.), and United Kingdom
Patent No. 498,485. U.S. Patent No. 5,352,342 to Riffe, which issued on October 4, 1994 and is
30 entitled "Method And Apparatus For Preventing Corrosion Of Metal Structures", describes
using electromotive forces upon a zinc solvent containing paint. U.S. Patent Nos. 5,700,523,
and 5,451,431; and German Patent No. 93115628 describe processes for using alkaline meta-
silicates to treat metallic surfaces. All of the aforementioned patents, patent applications and
publications are hereby incorporated by reference.

35 **[0005]** There is a need in this art for an environmentally benign metal treatment (e.g.,
substantially chromate free) that imparts corrosion resistance to metallic surfaces.

CROSS REFERENCE TO RELATED AND COMMONLY ASSIGNED PATENTS AND PATENT APPLICATIONS

5 [0006] The subject matter herein is related to the following commonly assigned patents and patent applications: U.S. Patent Nos. 6,149,794; 6,258,243; 6,153,080; 6,322,687; 6,572,756B2 and U.S. Patent Application Serial Nos. 09/816,879; 09/775,072; 09/814,641; 10/211,051; 10/211,094; 10/211,029 and 10/359,402. The disclosure of the foregoing patents and patent applications is hereby incorporated by reference.

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SUMMARY OF THE INVENTION

[0007] Broadly, the instant invention relates to treating a silicate medium and using the treated medium for improving the surface of metallic or electrically conductive materials. The treated silicate medium can be employed in an electroless or electrolytic process.

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[0008] By "electroless" it is meant that the treated silicate medium is used in a metal or surface treatment process wherein no current is applied from an external source (a current may be generated in-situ due to an interaction between the metallic surface and at least one medium). By "electrolytic" or "electrodeposition" or "electrically enhanced", as used herein it is meant to refer to an environment created by introducing or passing an electrical current through a silicate containing medium while the metallic or electrically conductive surface contacts the silicate medium (but not in direct contact with an electrode). Electrolytic also means passing a current through a silicate medium while in contact with the electrically conductive substrate (or having an electrically conductive surface). By "metal containing", "metal", or "metallic", it is meant to refer to sheets, shaped articles, fibers, rods, particles, continuous lengths such as coil and wire, metallized surfaces or electrically conductive films, among other configurations that are based upon at least one metal and alloys including a metal having a naturally occurring, or chemically, mechanically or thermally modified surface. Typically a naturally occurring surface (e.g., a passivating film), upon a metal or metallized surface will comprise a thin film or layer

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30 comprising at least one oxide, hydroxides, carbonates, sulfates, chlorides, among others. The naturally occurring surface can be removed or modified by using the inventive process. The metal containing surface refers to a metal article or body as well as a non-metallic member having an adhered metal or a conductive layer. While any suitable surface can be treated by the inventive process, examples of suitable metal surfaces comprise at least one member selected

from the group consisting of galvanized surfaces, sheradized surfaces (e.g, mechanically plated), zinc, chromium, iron, steel and other iron alloys, brass, copper, nickel, tin, aluminum, lead, cadmium, magnesium, silver, barium, beryllium, calcium, strontium, cadmium, titanium, zirconium, manganese, cobalt, alloys thereof such as zinc-nickel alloys, tin-zinc alloys, zinc-cobalt alloys, zinc-iron alloys, among others.

[0009] In some cases, the metal surface has been pretreated with another metal or compound that can interact with the silicate medium. While any suitable pretreatment metal or compound can be used, examples of suitable pretreatments comprise at least one member selected from the group of aluminum, copper, tin, titanium, chromium, molybdenum, tungsten, vanadium, selenium, arsenic, antimony, gold, silver, nitrates, phosphates, organic precursors thereof, among others. In some cases, the pretreating metal is delivered to the metal surface via a carrier comprising at least one member selected from the group consisting of water, at least one silicate (e.g., sodium silicate), solvent or water dispersible polymers, electrically conductive polymers, among others.

[0010] If desired, the inventive process can be employed to treat a non-conductive substrate having at least one surface coated with a metal, e.g., a metallized polymeric article or sheet, ceramic materials coated or encapsulated within a metal, among others. Examples of metallized polymer comprise at least one member selected from the group of polycarbonate, acrylonitrile butadiene styrene (ABS), rubber, silicone, phenolic, nylon, PVC, polyimide, melamine, polyethylene, polypropylene, acrylic, fluorocarbon, polysulfone, polyphenylene, polyacetate, polystyrene, epoxy, among others. Conductive surfaces can also include carbon or graphite as well as conductive polymers (polyaniline for example).

[0011] The process of using the silicate medium is a marked improvement over conventional methods by obviating the need for solvents or solvent containing systems to form a corrosion resistant film or layer, e.g., a mineral layer. In contrast, to conventional methods the inventive process can be substantially solvent free. By "substantially solvent free" it is meant that less than about 5 wt.%, and normally less than about 1 wt.% volatile organic compounds (V.O.C.s) are present in the electrolytic environment. The inventive process is also a marked improvement over conventional methods by reducing, if not eliminating, chromate and/or phosphate containing compounds (and issues attendant with using these compounds such as waste disposal, worker exposure, among other undesirable environmental impacts). While the inventive process

can be employed to enhance chromated or phosphated surfaces, the inventive process can replace these surfaces with a more environmentally desirable surface (e.g., a treating a trivalent chromate containing surface with the inventive process). The inventive process, therefore, can be “substantially chromate free” and “substantially phosphate free” and in turn produce articles that are also substantially chromate (hexavalent and trivalent) free and substantially phosphate free. The inventive process can also be substantially free of heavy metals such as chromium, cobalt, lead, cadmium, barium, among others. By substantially chromate free, substantially phosphate free and substantially heavy metal free it is meant that less than 5 wt.% and normally about 0 wt.% chromates, phosphates and/or heavy metals are present in a process for producing an article or the resultant article.

[0012] The process of using the silicate medium can provide an improved surface upon metallic or electrically conductive materials. The improved surface can comprise a first film or layer (including a colloidal layer on a metal or conductive polymer), in contact with the surface, which may comprise a metal silicate and a second film or layer upon the first that comprises at least one siliceous species (e.g., as described in Pages 83 – 94 of R. K. Iler, “The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry”, John Wiley & Sons, NY, 1979; Page 86 of Englehardt and Michel, “High Resolution Solid State NMR of Silicates and Zeolites” John Wiley & Sons, NY 1987; and Bass and Turner “Anion Distribution In Sodium Silicate Solutions. Characterization By ^{29}Si NMR And Infrared Spectroscopies And Vapor Phase Osmometry”, Journal of Physical Chemistry B, 1997 Vol 101(50), Pages 10638 to 10644; all hereby incorporated by reference). A silica containing film or coating can then be deposited upon the mono or disilicate film as a monomeric silica species (e.g., monomeric, dimer or oligomeric siliceous species). The silica containing film or coating may also include colloidal silica. The colloidal silica can be generated in situ (e.g., in an electrolytic process adjacent to the Helmholtz zone of the anode), or added to the silicate medium.

BRIEF SUMMARY OF THE DRAWINGS

[0013] Figure 1 is an SEM photomicrograph illustrating a potential defect that may be associated with the presence of hydrogen.

Figure 2 is a graphical representation of an NMR scan of a silicate medium before being used to treat metal components.

Figure 3 is a graphical representation of an NMR scan of the silicate medium of Figure 2 after treating metal components.

Figure 4 is a schematic drawing of a barrel apparatus for treating metal containing material in accordance with one aspect of the invention.

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DETAILED DESCRIPTION

[0014] The instant invention improves the previously disclosed processes by providing a silicate medium having a defined degree of polymerization and predetermined quantities of the desired silicate polymer (e.g., the instant invention can increase or decrease silicate
10 polymerization in order to obtain the desired concentration and type of silicate species). The inventive method comprises exposing the silicate medium to a current source for a time and under conditions sufficient to obtain the desired degree and concentration of polymerized silicate (e.g., oligomers ranging from monomeric [Q0] to tetramers [Q4] and colloids). The silicate medium can be used for improving the surface characteristics of metallic or electrically
15 conductive materials. The silicate medium can be exposed to a current source before, during or after contacting a metallic surface with the silicate medium. The degree of polymerization or speciation can be obtained or modified by varying the pH (e.g., by increasing the pH by adding a caustic compound such as sodium hydroxide, TMOH, among others), or, in the case of sodium silicate, by varying the ratio of sodium to silicon in the medium. The degree of polymerization
20 or speciation can also be modified by applying a current greater than the over potential of water so that hydrogen and oxygen are introduced into the silicate medium. The presence of hydrogen can increase the pH of the medium on a localized basis which in turn can cause silica depolymerization. The pH of the medium can also be increased by adding a caustic (e.g., sodium hydroxide, TMOH, etc.) which also can cause silica depolymerization and change the
25 concentration of siliceous species.

[0015] The compositions and processes described in the aforementioned Cross Referenced Patents And Patent Applications employ silicate containing mediums for improving the surface of a metal. These processes may form a mineral-like metal disilicate upon the metal surface and
30 a silica containing surface upon the disilicate. When a zinc surface is contacted with the silicate medium, a metal silicate, e.g., zinc silicate layer can formed by an interaction between certain oligimers or silicate species within the silicate medium. The silicate oligomers or silicate speciation can range from Q0 for monomeric, Q1 for dimeric silica groups, Q2 for trimeric

silica groups or species (that can include at anion) to Q4 for polymer. When interacting the silicate medium with a zinc surface, a silicate medium comprising Q0 and Q1 species is desirable. The instant invention can be employed in order to obtain a silicate medium having a desirable concentration of Q0 and Q1 species. The type and concentration of silicate species can vary depending upon the chemistry of the surface exposed to the silicate medium.

[0016] By treating or electrifying the silicate medium, the inventive method can reduce potential defects that can be associated with hydrogen (e.g., hydrogen embrittlement, cracking, non-uniform films, among potential defects associated with in-situ hydrogen evolution).

Further, a metallic surface that is treated by the inventive process can possess improved corrosion resistance, increased electrical resistance, heat resistance (including to molten metals), flexibility, resistance to stress crack corrosion, adhesion to sealer, paints and topcoats, among other properties.

[0017] When a silicate medium is employed in a cathodic electrolytic process for treating metallic surfaces, hydrogen gas can evolve upon the surface of the metallic surfaces while silica containing material is precipitated. Without wishing to be bound by any theory or explanation, it is believed that hydrogen bubbles can adversely affect the deposited silica or become trapped within the deposited silica. Referring now to Figure 1, Figure 1 is an SEM photomicrograph of what is believed to be a hydrogen bubble trapped within the deposited silica surface.

[0018] The instant method for treating the silicate medium can be practiced in the absence of the metal surface to be treated within the silicate medium. Therefore, in addition to providing a silicate medium having a desirable concentration of certain silicate oligomers or species, the instant invention can reduce the amount of hydrogen present in the silicate medium. While hydrogen may be undesirable in certain metal treating operations, hydrogen can be employed in the instant invention in order to obtain a desired silicate oligomer (e.g., monomer, dimer, etc) and concentration thereof (e.g., depolymerization of one silicate specie into a more desirable specie).

[0019] In one aspect of the invention, the silicate medium is present between or adjacent to an anode and a cathode under conditions sufficient to evolve hydrogen at the cathode and oxygen at the anode (e.g., at least equal to the overpotential of water when using an aqueous carrier). The anode and cathode can be fabricated from dimensionally stable materials or

materials that contribute desirable compounds or elements (e.g., zinc, nickel, iron, titanium, aluminum, among others). Examples of dimensionally stable materials comprise platinum, platinum plated niobium, platinum plated titanium, iridium oxide, among other materials stable at a pH of about 10-14.

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[0020] While the inventive process for treating the silicate medium can be practiced in any suitable manner non-limiting examples comprise treating the silicate in one vessel and pumping into a container for contacting metallic surfaces, a weir wherein the silicate is treated and then transferred to contact metallic surfaces, among other methods for treating the silicate medium separate from the metallic surface. If desired, the silicate can be treated in the same vessel as the metallic surfaces provided that hydrogen evolved from the silicate treatment has been substantially dehydrogenated or treated in order to substantially remove hydrogen from the medium (e.g., electrify the silicate solution for about 15 minutes, turn off power and then introduce metal components into the treated silicate solution, or electrify the silicate solution while in the presence of the metal components wherein the metal components are not in direct contact with the anode or cathode).

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[0021] If desired, at least one compound can be added to the silicate medium for improving the electrical conductivity of the medium. While any suitable compound or mixtures thereof can be added to the medium, an example of such a compound comprises TMOH (TMOH can also be employed as a stabilizer as described below in greater detail).

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[0022] In one aspect of the invention, the silicate treatment is conducted adjacent to a metal finishing operation (e.g., a barrel, basket or rack process for treating metallic components in the silicate medium). The silicate medium is withdrawn from a tank housing the medium, treated (e.g., electrified) in order to obtain the desired silicate polymerization and then reintroduced into the tank. Depending upon the condition of the silicate medium additional silicate, water, stabilizers, among other materials can be added to the silicate medium before, during or after being treated. If desired, the silicate medium can be filtered before, during or after treatment. Examples of suitable filtration systems comprises fibers, plates, media, among other filtration techniques. One suitable filtration example comprises passing the treated or untreated silicate medium through a media comprising diatomaceous earth (e.g., Auto-Vac System supplied by Alar Engineering, Mokane, Illinois).

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[0023] In one aspect of the invention, waste filtrate (e.g., used diatomaceous earth media or filtrate therefrom), or silicate medium that is undesirable for continued usage in treating metal surfaces is employed for buffering other metal plating wastes. After filtration, silicate medium acceptable for reuse is transported to a metal finishing tank, and unacceptable silicate medium
5 can be employed for treating metal plating waste streams. That is, the silicate medium has a basic pH that can be employed for buffering or precipitating solids from other metal plating processes (e.g., zinc plating or chromating waste streams). Employing the silicate medium for treating metal plating wastes reduces the overall cost of waste disposal while obtaining additional value from the silicate medium.

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[0024] In a further aspect of the invention, the metal part is treated while in the silicate medium without being in direct contact with an anode or a cathode (e.g., the metal part is within the silicate medium while a current is passed between an anode and a cathode within the medium). The metal part can be located between, or adjacent to the anode and/or cathode
15 thereby causing the metal part can become bipolar. By "bipolar" it is meant that a portion of the metal part functions as an anode or a cathode or both depending upon the relationship to the anode and cathode within the medium. The bipolar nature of the part can vary depending upon displacement of the metal part and/or electrodes. The spatial orientation can cause a portion of the metal part to be exposed to a cathodic environment and another portion of the same part to be
20 exposed to an anodic environment. This environment can be created by supplying DC or AC current to the anode and cathode.

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[0025] In another aspect of the invention, the silicate medium is treated and then introduced (e.g., pumped from a silicate treatment vessel) into a tank. Metal parts can be introduced into
25 the tank via a dip-spin basket or container having metal parts. The metal parts are exposed to the silicate medium for a time and under conditions sufficient to form the aforementioned improved silicate surface. If desired, the parts within the container can be activated or cleaned prior to exposure to the treated silicate medium. After removal from the silicate medium, the metal parts can be dried, coated with a sealer or topcoat, among other post-treatments.

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[0026] In some cases, the metal surface has been pretreated with another metal or compound that can interact with the silicate medium (e.g., an organic or inorganic film or layer containing the other metal is applied prior to contact with the silicate medium). While any suitable pretreatment metal or compound can be used, examples of suitable pretreatments comprise at

least one member selected from the group of aluminum (e.g., sodium aluminate, aluminum ammonium sulfate, aluminum fluoride, aluminum nitrate, aluminum phosphate, aluminum potassium sulfate, aluminum tartrate, among others), copper, tin, titanium (e.g., titanates), chromium (e.g., chromates), molybdenum (e.g., molybdates), tungsten, vanadium, selenium, arsenic, antimony, gold, silver, nitrates, phosphates (e.g., sodium ammonium phosphate), sodium acetate, sodium d-gluconate, inorganic or organic precursors thereof, at least one dopant (described below in greater detail), among others. In some cases, the pretreating metal is delivered to the metal surface via a carrier comprising at least one member selected from the group consisting of water, at least one silicate (e.g., sodium silicate), solvent or water dispersible polymers, among others. The concentration of the pretreating metal within the carrier (e.g., water) can vary but is normally about 0.001wt% to about 5.0wt.% (e.g., about 0.5 wt%). If desired, the pretreating metal is dissolved in at least one acid such as HCl, muratic, nitric, among others. In one aspect of the invention, an iron or a steel surface is pretreated with a phosphate (e.g., sodium polyphosphate), and then exposed to the silicate medium. The time and temperature of the pretreatment can vary depending upon the desired results and concentration of the metal (e.g., about 10 to about 90 seconds [normally about 30 seconds] under ambient conditions).

[0027] In one aspect, the surface is pretreated with an inorganic film or layer. The inorganic film or layer can comprise at least one of the aforementioned pretreating metals. The inorganic film or layer can be formed by any suitable process. An example of a suitable process comprises one of the processes disclosed in the aforementioned Cross-Referenced Patents And Patent Applications (e.g., a zinc or zinc alloy surface is exposed to an electrolytic silicate medium and then by the inventive process). Another example of a suitable process comprises forming a film or layer by contact with a potassium silicate containing solution.

[0028] Without wishing to be bound by any theory or explanation, it is believed that the film or layer formed by pretreating the surface can interact with the silicate medium (e.g., by ion exchanging). That is, it is believed that the film or layer can comprise metal species capable of ion exchange with the silicate medium (e.g., sodium silicate with zincate balanced sodium to form silica films/colloids).

[0029] The silicate medium can comprise water and at least one water soluble silicate such as at least one member selected from the group of sodium silicate, potassium silicate, lithium

silicate, ammonium silicate, tetramethylammonium silicates, tetraalkylammonium silicates, tetrabutylammonium silicates, among other silicates, siliceous species such as monomeric silica, oligomeric silica, polymeric silica, colloidal silica, among other water silicates and combinations thereof. While any suitable silicate can be employed, an example of suitable silicate comprises an oligomeric sodium silicate (e.g., available commercially from PQ Corporation as "D" grade sodium silicate). The oligomeric sodium silicate has a ratio of $\text{SiO}_2\text{wt.}/\text{Na}_2\text{Owt}$ of about 2.00 wherein the amount of $\text{NaOw/w\%}$ is about 13 to about 15 (e.g., about 14.7 $\pm$ 0.15) and the amount of $\text{SiO}_2\text{w/wt\%}$ is about 28 to about 30 (e.g., about 29.4). The amount of at least one water soluble silicate normally comprises about 1 to about 30wt.% of the first medium. If present in the silicate medium, the siliceous species (e.g., colloidal silica, monomeric or oligomeric silica-containing species) can have any suitable size and, normally, range from about 10 to 200 nanometers (e.g., about 15 to about 90nm). The silicate medium has a pH of about 10 to 14 (e.g., about 11.5).

[0030] In one aspect of the invention, a commercially available sodium silicate (N Grade sodium silicate which has $\text{SiO}_2\text{wt}/\text{Na}_2\text{Owt}$ ratio of 3:22 and a lower viscosity relative to oligomeric silicate [D-Grade]) is combined with D-grade sodium silicate in order to obtain the silicate medium. A blend of N-Grade and D-Grade sodium silicate can be employed to tailor the pH, degree and range of silicate polymerization, cost, among other parameters of the inventive silicate medium. The addition of at least one stabilizer such as TMOH (e.g., about 25wt.% to either N-grade or D-grade sodium silicate or mixtures thereof) can change the SiO_2 : alkali ratio of the medium thereby enhancing condensation of silica species onto a metal surface (e.g., a non-amphortic metal surface).

[0031] The silicate medium can further comprise at least one stabilizer. The stabilizer is employed for controlling or inhibiting growth of colloidal silica. Without wishing to be bound by any theory or explanation it is believed that dimer, trimer and other oligomeric forms present in the silicate medium can agglomerate or grow into colloidal silica. The stabilizer inhibits colloidal growth thereby maintaining the desired silicate polymerization within the silicate medium. While any suitable stabilizer can be employed, examples of such stabilizers comprise at least one member selected from the group of tetraalkylammonium hydroxides such as tetramethyl, tetraethyl, tetrapropyl and tetrabutyl ammonium hydroxides. The amount of stabilizer can vary depending upon the composition of the stabilizer, condition of silicate medium to which stabilizer is introduced, among other parameters (e.g., about 1% to 50wt.%

stabilizer). A non-limiting example of a stabilized silicate medium comprises a blend of 4.78 gal H₂O, 2.58 gal sodium silicate (N-Grade sodium silicate), and 2.24 gal tetramethylammonium hydroxide (TMAOH).

5 [0032] The specific electrolytic parameters used within the silicate medium depend upon the composition of the medium, extent to which the medium has been used for treating metallic materials, time, temperature, flow rate, among other parameters. Normally, the temperature of the medium ranges from about 25 to about 95 C (e.g., about 75C), the voltage from about 6 to 24 volts, with a silicate solution concentration from about 1 to about 15 wt.% silicate (e.g., about 10wt.% sodium silicate), the current density ranges from about 0.025A/in² and greater than 10 0.60A/in² and typically about 0.04A/in² (e.g., about 180 to about 200 mA/cm² and normally about 192 mA/cm²), contact time with the first medium from about 10 seconds to about 50 minutes and normally about 1 to about 15 minutes, and anode to cathode surface area ratio of about 0.5:1 to about 2:1 (e.g., 1:1). Depending upon whether a bipolar medium is desired, DC or 15 AC current can be supplied to the silicate medium.

[0033] In an aspect of the invention, the silicate medium can be modified to include at least one dopant material (e.g., to improve corrosion resistance, reduce torque tension, increase heat resistance, among other chemical and physical properties). Dopants can be added before, during 20 or after treatment in accordance with the instant invention (e.g., the previously described metal pretreatment). The dopants can be useful for building additional thickness of the film or layer obtained when exposing metallic articles to the silicate medium. The amount of dopant can vary depending upon the properties of the dopant and desired results. Typically, the amount of dopant will range from about 0.001 wt.% to about 5 wt.% (or greater so long as the deposition 25 rate is not adversely affected). Examples of suitable dopants comprise at least one member selected from the group of water soluble salts, oxides and precursors of tungsten, molybdenum, titanium (titanates), zircon, vanadium, phosphorus, aluminum (aluminates), iron (e.g., iron chloride), boron (borates), bismuth, gallium, tellurium, germanium, antimony, niobium (also known as columbium), magnesium and manganese, sulfur, zirconium (zirconates) mixtures 30 thereof, among others, and usually, salts and oxides of aluminum and iron, and other water soluble or dispersible monovalent species. The dopant can comprise at least one of molybdenic acid, fluorotitanic acid and salts thereof such as titanium hydrofluoride, ammonium fluorotitanate, ammonium fluorosilicate and sodium fluorotitanate; fluorozirconic acid and salts thereof such as H₂ZrF₆, (NH₄)₂ZrF₆ and Na₂ZrF₆; among others. Alternatively, dopants can

comprise at least one substantially water insoluble material such as electrophoretic transportable polymers, PTFE, boron nitride, silicon carbide, silicon nitride, aluminum nitride, titanium carbide, diamond, titanium diboride, tungsten carbide, metal oxides such as cerium oxide, powdered metals and metallic precursors such as zinc, among others.

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[0034] The aforementioned dopants can also be employed for modifying the chemistry of the silicate medium and/or physical properties of the silicate film or layer formed on the metallic surface, as a diluent for the medium, among others. Additional examples of such dopants are iron salts (ferrous chloride, sulfate, nitrate), aluminum fluoride, fluorosilicates (e.g., K_2SiF_6),
10 fluoroaluminates (e.g., potassium fluoroaluminate such as $K_2AlF_5 \cdot H_2O$), mixtures thereof, among other sources of metals and halogens. The dopant materials can be introduced to the metal surface in pretreatment steps and/or post treatment steps (described below in greater detail), and/or by alternating exposing the metal surface to solutions of dopants and solutions of the silicate medium.

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[0035] The silicate medium can also be modified by adding at least one diluent. Similar to the dopant, the diluent can be added before, during or after treating the silicate medium in accordance with the instant invention. Examples of suitable diluent comprise at least one member selected from the group of sodium sulphate, surfactants, de-foamers, colorants/dyes,
20 conductivity modifiers, among others. The diluent (e.g., sodium sulfate) can be employed for reducing the affects of contaminants entering the medium, reducing bath foam, among others. When the diluent is employed as a defoamer, the amount normally comprises less than about 5 wt.% of the medium, e.g., about 1 to about 2 wt.%.

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[0036] In one aspect of the invention, exposing metallic materials to the treated silicate medium of the invention is preceded and/or followed by procedures known in this art such as cleaning or rinsing, e.g., immersion/spray within the treatment, sonic cleaning, double counter-current cascading flow; alkali or acid treatments, among other treatments. By employing a suitable post-
or pre-treatment the solubility, corrosion resistance (e.g., reduced white rust formation when
30 treating zinc containing surfaces), sealer and/or topcoat adhesion, among other properties of treated metallic surface formed by the inventive method can be improved. If desired, the post-treated surface can be sealed, rinsed and/or topcoated, e.g., silane, epoxy, latex, fluoropolymer, acrylic, among other coatings.

[0037] In one aspect of the invention, a pre-treatment comprises exposing the metallic surface or substrate to be treated to at least one of an acid, oxidizer, a basic solution (e.g., potassium or sodium hydroxide) among other compounds. The pre-treatment can be employed for removing excess oxides or scale, equipotentialize the surface for subsequent mineralization treatments, hydroxylize, convert the surface into a silicate containing or silica containing precursor, among other benefits. Conventional methods for acid cleaning metal surfaces are described in ASM, Vol. 5, Surface Engineering (1994), and U.S. Patent No. 6,096,650; hereby incorporated by reference.

[0038] In another aspect of the invention, the metal surface is pre-treated or cleaned electrolytically by being exposed to an anodic environment. That is, the metal surface is exposed to the medium wherein the metal surface is the anode and a current is introduced into the medium. If desired, anodic cleaning can occur within the silicate medium. By using the metal as the anode in a DC cell and maintaining a current of about 10A/ft² to about 150A/ft², the process can generate oxygen gas. The oxygen gas agitates the surface of the workpiece while oxidizing the substrate's surface. The surface can also be agitated mechanically by using conventional vibrating equipment. If desired, the amount of oxygen or other gas present during formation of the mineral layer can be increased by physically introducing such gas, e.g., bubbling, pumping, among other means for adding gases.

[0039] In a further aspect of the invention, the metal part is pretreated to have a darkened appearance. The darkened part can be treated in accordance with the instant invention (e.g., exposure to a silicate medium and/or bipolar environment). The darkened part, which has been exposed to the instant silicate medium, provides a desirable surface for secondary coatings; especially for dark or black secondary coatings (e.g., cathodic lacquers such as those commercially available from PPG). Examples of suitable darkening processes comprise exposing the metal surface to a dye, anodizing, chemical reactants (e.g., molybdate compounds), among other process effective at causing the metal surface to have a relatively dark surface. A suitable anodizing process is described in "Zinc Anodizing" by Wolfgang Paatsch, June 1995-Metal Finishing; hereby incorporated by reference. Commercial darkening compounds are available from Jost Chemicals as Insta-Blak Z360. In most cases it is desirable to pre-treat or clean the parts prior to the darkening process (e.g., by immersion with dilute nitric acid, ammonium citrate, citric acid, among others). While any darkening process can be employed, one example comprises exposing a zinc containing part to an electrolyte comprising 20g/L

NaOH and 5g/L NaClO₂ and applying an AC current having a current density of about 40A/dm². The electrolyte is maintained at a temperature of about 30C and the process operated for about 40 minutes. The darkened and silicate treated parts can be dried at a temperature and time sufficient to remove water (e.g., for about 4 minutes at 120C). Without wishing to be
5 bound by any theory or explanation, it is believed that combining a darkening process with exposure to the silicate medium can form a zinc chloride phase (e.g., ZnCl₂-4Zn(OH)₂) that in turn imparts improved corrosion resistance.

[0040] If desired, the method for treating metallic materials can include a thermal post-treatment
10 following exposure to the silicate medium. The metal surface can be removed from the medium, dried (e.g., at about 120 to about 150C for about 2.5 to about 10 minutes), rinsed in deionized water and then dried. The dried surface may be processed further as desired; e.g. contacted with a sealer, rinse or topcoat. Typically the amount of heating in drying steps herein is sufficient to consolidate or densify the inventive surface without adversely affecting the physical properties
15 of the underlying metal substrate. Heating can occur under atmospheric conditions, within a nitrogen containing environment, among other gases. Alternatively, heating can occur in a vacuum. The surface may be heated to any temperature within the stability limits of the surface coating and the surface material. Typically, surfaces are heated from about 75° C to about 250° C, more typically from about 120° C to about 200° C. If desired, the heat treated component can
20 be rinsed in water to remove any residual water soluble species and then dried again (e.g., dried at a temperature and time sufficient to remove rinse water).

[0041] In one aspect of the invention, a post treatment following exposure to the treated silicate medium comprises exposing the substrate to a source comprising at least one acid source or
25 precursors thereof. Examples of suitable acid sources comprise at least one member chosen from the group of phosphoric acid, hydrochloric acid, molybdic acid, silicic acid, acetic acid, citric acid, nitric acid, hydroxyl substituted carboxylic acid, glycolic acid, lactic acid, malic acid, tartaric acid, ammonium hydrogen citrate, ammonium bifluoride, fluoboric acid, fluorosilicic acid, glacial acetic acid, among other acid sources effective at improving at least one property of
30 the treated metal surface. The pH of the acid post treatment may be modified by employing at least one member selected from the group consisting of ammonium citrate dibasic (available commercially as Citrosol® #503 and Multiprep®), fluoride salts such as ammonium bifluoride, fluoboric acid, fluorosilicic acid, among others. The acid post treatment can serve to activate the surface thereby improving the effectiveness of rinses, sealers and/or topcoatings (e.g., surface

activation prior to contacting with a sealer can improve cohesion between the surface and the sealer thereby improving the corrosion resistance of the treated substrate). The acid post treatment can also function to reduce any adverse interaction between the treated surface and an overlying sealer or coating that is sensitive to a basic pH. Normally, the acid source will be water soluble and employed in amounts of up to about 15 wt.% and typically, about 1 to about 5 wt.% and have a pH of less than about 5.5.

[0042] If desired, after contacting the silicate medium the surface can be rinsed; typically after being dried. By "rinse" it is meant that an article or a treated surface is sprayed, dipped, immersed or other wise exposed to the rinse in order to affect the properties of the treated surface. For example, a surface treated by the inventive process is immersed in a bath comprising at least one rinse. In some cases, the rinse can interact or react with at least a portion of the treated surface. Further the rinsed surfaced can be modified by multiple rinses, heating, topcoating, adding dyes, lubricants and waxes, among other processes. Examples of suitable compounds for use in rinses comprise at least one member selected from the group of titanates, titanium chloride, tin chloride, zirconates, zirconium acetate, zirconium oxychloride, fluorides such as calcium fluoride, tin fluoride, titanium fluoride, zirconium fluoride; cuprous compounds, ammonium fluorosilicate, metal treated silicas (e.g., Ludox® products such as Ludox® CL), nitrates such as aluminum nitrate; sulphates such as magnesium sulphate, sodium sulphate, zinc sulphate, and copper sulphate; lithium compounds such as lithium acetate, lithium bicarbonate, lithium citrate, lithium metaborate, lithium vanadate, lithium tungstate, silanes, among others. The rinse can further comprise at least one organic compound such as vinyl acrylics, fluorosurfactants, polyethylene wax, among others. One specific rinse comprises water, water dispersible urethane, and at least one silicate, e.g., refer to commonly assigned U.S. Patent No. 5,871,668; hereby incorporated by reference. While the rinse can be employed neat, normally the rinse will be dissolved, diluted or dispersed within another medium such as water, organic solvents, among others. While the amount of rinse employed depends upon the desired results, normally the rinse comprises about 0.1wt% to about 50 wt.% of the rinse medium. The rinse can be employed as multiple applications and, if desired, heated. Moreover, the aforementioned rinses can be modified by incorporating at least one dopant, e.g. the aforementioned dopants. The dopant can employed for interacting or reacting with the treated surface. If desired, the dopant can be dispersed in a suitable medium such as water and employed as a rinse.

[0043] In one aspect, a post-treatment comprises exposing the treated surface to at least one compound that absorbs, adsorbs or chemically removes water from the treated surface. While any suitable compound or method can be employed, an example comprises rinsing the treated surface with at least one silane containing solution. Water can be removed from the treated surface, in the case of barrel processed parts, by spinning the parts, rinsing in a silane containing solution and spinning again.

[0044] If desired, after an optional rinsing step at least one secondary coating can be applied.

Examples of suitable such coatings comprise at least one member selected from the group of Aqualac® (urethane containing aqueous solution), W86®, W87®, B37®, T01®, E10®, B17, B18 among others (a heat cured coating supplied by the Magni® Group), JS2030S (sodium silicate containing rinse supplied by MacDermid Incorporated), JS2040I (a molybdenum containing rinse also supplied by MacDermid Incorporated), EnSeal® C-23 (an acrylic based coating supplied by Enthone), EnSeal® C-26, Enthone® C-40 (a pigmented coating supplied Enthone), Microseal®, Paraclene® 99 (a chromate containing rinse), EcoTri® (a silicate/polymer rinse), MCI Plus OS (supplied by Metal Coatings International), silanes (e.g., at least one of Dow Corning Z-6040Z6137 and QP8-5314, and Gelest SIA 0610.0), tetra-ortho-ethyl-silicate (TEOS), bis-1,2-(triethoxysilyl) ethane (BSTE), vinyl silane or aminopropyl silane, epoxy silanes, vinyltriactosilane, alkoxysilanes, among other organo functional silanes), ammonium zirconyl carbonate (e.g., Bacote 20), urethanes (e.g., Agate L18), acrylic coatings (e.g., IRILAC®), e-coats (e.g., PPG Powercron), silanes including those having amine, acrylic and aliphatic epoxy functional groups, latex, urethane, epoxies, silicones, alkyds, phenoxys resins (powdered and liquid forms), radiation curable coatings (e.g., UV curable coatings), lacquer including cathodically applied lacquers, shellac, linseed oil, torque tension modifiers (e.g., TNT15 from MacDermid), commercially available coatings such as Technicaq 330, Techniseal 448 and Briteguard RP-90, among others. Coatings can be solvent or water borne systems. These coatings can be applied by using any suitable conventional method such as immersing, dip-spin, spraying, among other methods. The secondary coatings can be cured by any suitable method such as UV exposure, heating, allowed to dry under ambient conditions, among other methods. An example of UV curable coating is described in U.S. Patent Nos. 6,174,932; 6,057,382; 5,759,629; 5,750,197; 5,539,031; 5,498,481; 5,478,655; 5,455,080; and 5,433,976; hereby incorporated by reference. The secondary coatings can be employed for imparting a wide range of properties such as improved corrosion resistance to the underlying mineral layer, reduce torque tension, a temporary coating for shipping the treated work-piece, decorative finish,

static dissipation, electronic shielding, hydrogen and/or atomic oxygen barrier, among other utilities. The treated and coated metal, with or without the secondary coating, can be used as a finished product or a component to fabricate another article.

- 5 [0045] The thickness of the rinse, sealer and/or topcoat can range from about 0.00010 inch to about 0.00025 inch. The selected thickness varies depending upon the end use of the coated article. In the case of articles having close dimensional tolerances, e.g., threaded fasteners, normally the thickness is less than about 0.00005 inch.
- 10 [0046] In another aspect of the invention, a metal part is exposed to a silicate medium and then coated with at least two secondary coatings. If desired, the silicate medium can be operated in a bipolar environment. One example comprises exposing zinc plate parts (e.g., rivets) to a bipolar silicate medium for about 3.5 minutes, drying the parts, rinsing with water, drying, applying a first coating comprising sodium silicate with aluminum and magnesium (e.g., available
- 15 commercially from A-Bright as Briteguard RP-90), drying the first coating, applying a second coating comprising at least one silane (e.g., DowCorning Z6137), drying the second coating and applying a third coating comprising a polymer and wax composition (e.g., available commercially as MacDermid TNT). This multiple coating system can achieve improved corrosion resistance when measuring in accordance with ASTM B-117 (e.g., greater than 200
- 20 hours until appearance of white rust or zinc corrosion products).

- [0047] In another aspect of the invention, the metal part is exposed to a silicate medium and then electrolytically coated. Examples of electrolytically coating comprise at least one of e-coats, cathodic lacquers (e.g., commercially available as PPG® Black Powerseal XL), among others.
- 25 If desired, the metal part can be darkened prior to exposure to the silicate medium. That way a darkened part is provided which can be coated with a dark or black coating (e.g., to ensure that a relatively light colored surface is not visible through a relatively dark coating).

- [0048] Exposure to the treated silicate medium of the invention can provide a surface that
- 30 improves adhesion between a treated substrate and an adhesive. Examples of adhesives comprise at least one member selected from the group consisting of hot melts such as at least one member selected from the group of polyamides, polyimides, butyls, acrylic modified compounds, maleic anhydride modified ethyl vinyl acetates, maleic anhydride modified polyethylenes, hydroxyl terminated ethyl vinyl acetates, carboxyl terminated ethyl vinyl

acetates, acid terpolymer ethyl vinyl acetates, ethylene acrylates, single phase systems such as dicyanamide cure epoxies, polyamide cure systems, lewis acid cure systems, polysulfides, moisture cure urethanes, two phase systems such as epoxies, activated acrylates polysulfides, polyurethanes, among others. Two metal substrates having surfaces treated in accordance with the inventive process can be joined together by using an adhesive. Alternatively one substrate having the inventive surface can be adhered to another material, e.g., joining treated metals to plastics, ceramics, glass, among other surfaces. In one specific aspect, the substrate comprises an automotive hem joint wherein the adhesive is located within the hem.

[0049] The inventive process can be used for treating a wide range of metal surfaces such as discrete components in a barrel, larger or unusual shaped components on a rack, continuous strips, among other surfaces. For example, the inventive process can be used for treating assemblages (e.g., welded structures such as a vehicle frame) in a method comprising placing the assemblage onto a rack that transports the assemblage through the method. The assemblage is cleaned (e.g., with a dilute acid), rinsed with water, hydroxylized by immersion within a caustic (e.g., dilute sodium hydroxide), rinsed, and immersed into the inventive silicate medium (i.e., a previously electrified silicate medium). If desired, a coating can be applied (e.g., a sealer comprising zinc silicate and at least one silane), upon the treated surface, and optionally a second coating comprising an e-coat, a powder paint, among others, can be applied upon the first coating

EXAMPLES

[0050] The following Examples are provided to illustrate certain aspects of the invention. These Examples shall not limit the scope of any claims appended hereto.

EXAMPLE 1

[0051] This Example illustrates the polymerized silicate species that interacts with a zinc metal surface. A silicate medium was used for processing zinc components in accordance with aforementioned U.S. Patent Application Serial No. 09/814,641; incorporated by reference. The silicate medium was evaluated before and after treating the zinc components in accordance with conventional ^{29}Si nuclear magnetic resonance (NMR) methods.

[0052] Referring now to the Drawings, Figure 2 illustrates the NMR spectra of the silicate medium before treating zinc components and Figure 3 illustrates the NMR spectra of the silicate

medium following zinc component treatment. Figures 2 and 3 include the spectral trace, integrated peak areas and individual peak data. The relative amounts of different Si-O linkages in a sample are determined by comparing the integrated peak areas.

- 5 [0053] In each of the spectra there is a series of S- shaped curves associated with a number. For example, in the spectrum of Figure 2, the integrated peak area for the -72.25 ppm peak (assigned to Q^0 , monomer) is 10.00. There is also a series of S-shaped curves ranging from about -86 ppm to -130 ppm which include three types of linkages. In order to obtain the integrated area for polymer, Q^4 , it was necessary to subtract the integrated areas for the other two
- 10 linkage types. Thus the integrated area for polymer in this sample is $144.02-42.01-29.61= 72.2$. The following table summarizes the integrated peak area data.

Linkage Type	Integrated Area- used medium	% Linkage Type- used medium	Integrated Area- new medium	% Linkage Type- new medium
Q^0 , monomer	10.0	6.0	10.0	6.6
Q^1 , end groups and Q_{cy3}^2 , middle 3-ring groups	12.44	7.5	13.35	8.9
Q_{lin}^2 , Q_{cy4}^2 , middle linear and 4-ring groups, Q_{cy3}^3 , branching 3-ring groups	29.61	17.8	31.71	21.1
Q_{cy4}^3 , branching 4-ring groups	42.01	25.3	44.54	29.6
Q^4 polymer	72.2	43.4	50.76	33.7
Sum of integrated intensities	166.26		150.36	

- [0054] A description of the different linkage types is found in Engelhardt and Michel, " High
- 15 Resolution Solid State NMR of Silicates and Zeolites, p. 76; hereby incorporated by reference.

- [0055] The data show that the used sample has more polymer and less of the smaller anions than the new sample. The data also show that Q^0 and Q^1 species are more actively involved in an interaction or a reaction with the zinc surfaces (Q^0 can react with zinc to form willimite and Q^1
- 20 can react with zinc to form hemimorphite type of zinc disilicate).

EXAMPLE 2

- [0056] This Example demonstrates treating the silicate medium prior to contacting metal surfaces in order to obtain a medium having desirable silicate oligimers and using the treated
- 25 medium to form a mineral-like silicate layer.

[0057] The silicate medium was treated by placing an inert anode and inert cathode in an inert fixture. Specifically, platinum clad niobium panels of substantially the same dimensions were

used for both the anode and the cathode. The fixture was fabricated from polypropylene and installed in a 4 liter beaker set on a hot plate. A parastolic pump was used to transfer the treated silicate medium (e.g., at least partially depolymerized sodium silicate) to a second beaker. The second beaker was used to expose zinc plated parts to the cathodic process described in U.S.

5 Patent Application No. 09/814,641; hereby incorporated by reference. The second bath was also placed on a hot plate. Both baths were maintained at 80° C.

[0058] The process was run in both sodium silicate as well as potassium silicate with varied sodium to silica oxide ratios.

10

[0059] The corrosion resistance of parts processed in accordance with the above process were tested by neutral salt fog testing per ASTM B117. The corrosion resistance was increased from 24 hours (formation of first white rust corrosion) to 48 hours.

15

EXAMPLE 3

[0060] This Example illustrates a barrel apparatus that can be used for treating metal parts in a bipolar silicate medium. Referring now to the drawings, Figure 4 illustrates a process barrel that is constructed from materials known in the zinc plating art (e.g., polypropylene). The process barrel is at least partially filled with metallic parts such as rivets, fasteners, among other
20 components conventionally used in barrel metal finishing, and then inserted into a process tank containing a silicate medium. A dimensionally stable anode (e.g., constructed from platinum plated niobium mesh) is located between the process barrel and the sides of the process tank. The anode and process barrel are connected to a commercially available rectifier in a manner such that a cylindrical mesh located about the center longitudinal axis of the barrel functions as a
25 cathode. A non-conductive mesh is located concentrically about the cathode mesh in order to allow contact between the cathode mesh and the silicate medium while preventing parts from contacting the cathode mesh (e.g., during rotation of the barrel). When power is supplied to the barrel, anode and cathode, the metal parts are rotated within a bipolar silicate medium.

30

EXAMPLE 4

[0061] This Examples demonstrates a bipolar process for treating zinc plated tubular metal rivets. The rivets measured about 0.75 inch by about 1.0 inch. The rivets were pretreated or cleaned by:

- 1) washing with soap and water,
- 2) agitate within 0.5% nitric acid at room temperature for 30 seconds,
- 3) rinse for 10 seconds in de-ionized water,
- 4) agitate within 38% NaOH at 75C for 30 seconds,
- 5) rinse with 10 seconds with warm tap water.

A silicate medium was established by adding 10 vol% N-grade sodium silicate to a bath heated to 75C. The bath measured about 4 by about 4 inches. An anode and cathode each comprising 3 x 6 inch dimensionally stable mesh panels were inserted into the bath. The pretreated rivets were placed in a polypropylene and immersed in the silicate medium. Current was supplied to the anode and cathode at about 7-9A which achieved a current density of about 0.5 ASI at 15V. The rivets were maintained in the silicate medium for about 15 minutes. The rivets were dried under atmospheric conditions in a furnace at 80C for 4 minutes. The dried rivets were rinsed with tap water for 10 seconds and oven dried again.

EXAMPLE 5

[0062] Example 4 was repeated except that the silicate medium was treated with electricity for 15 minutes at 0.5 ASI in accordance with Example 2 prior to introducing the rivets. The rivets were immersed within the treated silicate medium having a temperature of about 80C for a period of about 2 minutes.

EXAMPLES 6-10

[0063] These examples demonstrate applying a topcoat upon articles treated in accordance with the inventive process. The articles comprised zinc plated rivets measuring 1/8 inch tubular shank with a 3/4 inch dia. head, and the topcoat comprised a black cathodic lacquer (available commercially as PPG Black Powerseal XL). Prior to conducting the inventive process, the articles were chemically darkened by exposure to one of the following processes: ammonium molybdate rinse, commercially available solution (e.g., Insta-Blak Z-360), and anodization. For purposes of comparison, zinc plated rivets, which were not processed in accordance with the inventive process, were coated with the cathodic lacquer. The corrosion performance of all rivets was tested in accordance with ASTM B-119 and the first occurrence of white rust (zinc corrosion products) was recorded (in general a relatively long period of testing time before

occurrence of white rust corresponds to a more corrosion resistance article). The average first white rust for the control or comparison rivets was 538 hours.

[0064] The following Examples list each step of the Process that was used to treat the rivets and the length of time for each Process.

Example 6

Process	Time
A. Pretreat – Soap and Water (Clean)	1.0 Min.
Rinse (3X)	10 Sec/Each
B. Activate - .01% Sulfuric Acid	30 Sec
Rinse (3X)	10 Sec/Each
C. Blacken – 12g/l Ammonium Molybdate 5 m/l Ammonia	45 Min
D. Dry – Spin Dry	
E. Silicate Medium - 10% N Grade Sodium Silicate Solution/D.I. Water @ 75° C pH 11.07, SG=1.047 Electrify Medium with 7-9 Amp @ 15.7 Volts--Shut Off Power Then Drop Workpiece Into Medium and Rotate Barrel	15 Min. 2 Min
F. Drying – None	
G. Topcoat – PPG Cathodic Black Lacquer	

ASTM B-117 Performance: First White Rust 864 hours

Example 7

Process	Time
A. Pretreat – E-Kleen 148 Solution (500 ml) @37° C	30 Sec
Rinse (3X)	10 Sec/Each
B. Activate – E-Kleen 154 Solution @ Ambient	30 Sec
Rinse (3X)	10 Sec/Each
C. Blacken – Insta-Blak Z-360	5 Min
Rinse	5 Min
D. Silicate Medium -- 10% N Grade Sodium Silicate Solution/D.I. Water @ 75° C pH 11.07, SG=1.047 Electrify Medium With 7-9 Amp @ 15.7 Volts Shut Off Power And Then Drop Workpiece into Medium Rotate Barrel	15 Min 2 Min
E. Drying – 120°C	4 Min
F. Topcoat- PPG Cathodic Black Lacquer	

ASTM B-117 Performance: First White Rust 504 hours

Example 8

	<u>Process</u>	<u>Time</u>
5	A. Pretreat – Soap and Water (Clean)	1.0 Min
	Rinse (3X)	10 Sec/Each
	B. Activate – 1% Sulfuric Acid	30 Sec
10	C. Blacken – Anodize in NaOH (60g/l @ 35-40°C @ 1.2 Amps, 3 Volts	30 Min
	D. Dry – Spin Dry	30 Sec
	E. Silicate Medium – 17.5% D Grade Sodium Silicate Solution/D.1. Water @ 75°C, pH 11.84,	
15	Electrify Medium with 1.1 Amps, 2 Volts	15 Min
	Shut Off Power	
	Drop Work Piece Into Medium	
	Rotate Barrel	2 Min
20	F. Drying – 80°C	4 Min
	G. Topcoat – P.P.G. Cathodic Black Lacquer	

ASTM B-117 Performance: First White Rust 826 hours

Example 9

	<u>Process</u>	<u>Time</u>
25	A. Pretreat – Soap and Water (Clean)	1 Min
	Rinse (3X)	10 Sec/Each
	B. Activate – 0.1% Sulfuric Acid	30 Sec
30	Rinse (3X)	10 Sec/Each
	C. Blacken – 12 g/l Ammonium Molybdate And 5 ml Ammonia	45 Sec
	D. Dry – Spin Dry	30 Sec
	E. Silicate Medium --10% N Grade Sodium Silicate/D.I. Water S.G. 1.044	
35	Electrify Medium @ 75°C, 7-8 Amp, 15.7 Volts	15 Min
	Shut Off Power	
40	Drop Workpiece Into Bath	
	Rotate Barrel	2 Min
	F. Drying – 4 Min @ 120° C	
	G. Topcoat – P.P.G. Cathodic Black Lacquer	

ASTM B-177 Performance: First White Rust 522 hours

Example 10

	<u>Process</u>	<u>Time</u>
50	A. Pretreat – Soap and Water (Clean)	1 Min
	Rinse (3X)	10 Sec/Each

	B. Activate – 0.1% Sulfuric Acid	30 Sec
	Rinse (3X)	10 Sec/Each
	C. Blacken – Anodize in NaOH (60g/l @ 35-40° C) @ 1.2 Amps, 3 Volts	30 Min
5	D. Dry – Spin Dry	30 Sec
	E. Silicate Medium --10% N Grade Sodium Silicate/D.I. Water	
	S.G. 1.044, Electrify Medium	15 Min
	@ 75° C, 7-8 Amp, 15.7 Volts	
10	Shut Off Power	
	Drop Workpiece Into Medium	
	Rotate Barrel.	2 Min
	F. Dry – None	
15	G. Topcoat – P.P.G. Cathodic Black Lacquer	
	ASTM B-117 Performance: First White Rust 828 hours	

[0065] Examples 6-10 illustrate that, in some cases, the instant invention can be employed along with a blackening or darkening pretreatment for improving the corrosion resistance of topcoated articles as well as achieving a substantially uniform black with one coat of lacquer

EXAMPLE 11

[0066] Example 4 was repeated with the exception that the rivets were exposed to a metal pretreatment prior to being introduced into the silicate medium. The metal pretreatment comprised dipping the rivets into a solution comprising sodium silicate, magnesium and aluminum (e.g., available commercially as RP-90 from A-Brite Company, Dallas, Texas), and spin drying. The pretreated rivets were then exposed to the silicate medium for a period of about 7.5 minutes while applying a cathodic current to rivets. The rivets were dried, rinsed and dried in accordance with Example 4. The corrosion resistance of the dried rivets was tested in accordance with ASTM B-117 and achieved an average of 192 hours before the first occurrence of white rust (zinc corrosion products).

EXAMPLE 12

[0067] Example 11 was repeated with the exception that the metal pretreatment was thickened by adding an aliphatic polymer with carboxylic acid groups (CARBOPOL supplied by B.F. Goodrich), and the electrolytic treatment in the silicate medium was for 3.5 minutes. The corrosion resistance of the dried rivets was tested in accordance with ASTM B-117 and achieved an average of 234 hours before the first occurrence of white rust (zinc corrosion products).

EXAMPLE 13

[0068] Example 11 was repeated with the exception that the metal pretreatment comprised sodium aluminate, sodium hydroxide and water (20ml of 5wt.% sodium hydroxide and 14 grams of sodium aluminate), and the electrolytic treatment in the silicate medium was for 3.5 minutes. The corrosion resistance of the dried rivets was tested in accordance with ASTM B-117 and
5 achieved an average of 373 hours before the first occurrence of white rust (zinc corrosion products).

EXAMPLE 14

[0069] In this Example, Example 4 was repeated with the exception that the rivets were not pretreated/cleaned and were exposed to an acidic post-treatment. Rivets were treated with the
10 process of Example 4 for a period of thirty (30) seconds, spun dry, rinsed in deionized water and then immersed in each of the following dilute acidic solutions:

Citric acid (pH 2.2, 5ml acid in 200ml deionized water), oxalic acid (pH 3.0, 5ml oxalic acid and 200ml deionized water) and glacial acetic acid (pH 3.4, 5ml glacial acetic acid and 2liters
15 deionized water). The corrosion resistance of the acid treated rivets was tested in accordance with ASTM B-117 and the following number of hours passed without the appearance of white rust (zinc corrosion products): citric = 72 hrs, oxalic = 24 hrs and glacial acetic acid = 72hrs.

EXAMPLE 15

[0070] This Example demonstrates using the inventive process as a post-treatment for the electrolytic process described in the aforementioned Cross Referenced Related Patents and Patent Applications. The rivets of Example 4 were cleaned with soap and water and then dipped in dilute nitric acid. The rivets were then introduced into a silicate medium of Example 4 and a charge ranging from 7 to 9 amps at 15.7 V was applied with the rivets corresponding to the
20 cathode. The current was disconnected and the rivets were removed from the silicate medium, and then reintroduced into the silicate medium for a period of 15 minutes (without current being applied). The rivets were dried for 4 minutes at 80C, rinsed in deionized water and dried again. The corrosion resistance of the dried rivets was tested in accordance with ASTM B-117 and achieved an average of 160 hours before the first occurrence of white rust (zinc corrosion
25 products).

EXAMPLE 16

[0071] This Example demonstrates using a pretreatment and a post-treatment for the inventive process. The rivets of Example 4 were cleaned in soap and water and rinsed three times in

deionized water. The rinsed rivets were then dipped three times in dilute nitric acid and rinsed three times in deionized water. The rinsed rivets were then pretreated by being immersed in sodium aluminate (38% sodium aluminate liquid [supplied by UALCO], 10:1 dilution with deionized water). The pretreated rivets were then spun dry. The dried rivets were then treated in accordance with Example 4 but with a bath comprising sodium silicate having a 6:1 alkaline to silicate ratio (D Grade sodium silicate from PQ Corporation). The rivets were then spun dry for 2 minutes at a temperature of 120F. The dried rivets were then immersed in a solution comprising colloidal silica (10wt.% Ludox CL). The rivets were then dried for 2 minutes at a temperature of 120F. A secondary coating or sealer comprising silicate (RP 90 supplied by A Brite) was applied onto the dried rivets. The rivets were dried for 3 minutes at 65 C. The corrosion resistance of the dried rivets was tested in accordance with ASTM B-117 and achieved an average of 188 hours before the first occurrence of white rust (zinc corrosion products).

EXAMPLE 17

[0072] This example demonstrates using a pretreatment prior to exposure to a silicate bath of the instant invention. Rivets were pretreated in accordance with the description set forth in following Tables 1 and 2. The sodium silicate bath of Example 4 was electrified prior to introducing the pretreated rivets. The corrosion resistance of the rivets was tested in accordance with ASTM B-117. The resistance of the rivets to white rust (zinc corrosion products) is set forth in Table 1, and the resistance of the rivets to the formation of red rust (underlying iron corrosion) is set forth in Table 2.

TABLE 1

ID	Description	Max	Min	Average	Std. Dev	CV	Range	SAMPLE 1	SAMPLE 2	SAMPLE 3	SAMPLE 4	SAMPLE 5	SAMPLE 6	SAMPLE 7	SAMPLE 8
Group A1	Sodium Acetate, 0.001 wt%	72	48	60	12.8	0.21	24	48	72	48	48	72	72	72	48
Group A2	Sodium Acetate, 0.5 wt%	96	24	48	22.2	0.46	72	48	48	24	96	48	48	48	24
Group A3	Sodium Acetate, 5.0 wt%	96	48	66	17.0	0.26	48	48	48	48	96	72	72	72	72
Group B1	Aluminum Ammonium Sulfate, 0.001 wt%	72	48	51	8.5	0.17	24	48	48	48	48	48	48	72	48
Group B2	Aluminum Ammonium Sulfate, 0.5 wt%	48	24	42	11.1	0.26	24	48	24	48	48	48	48	48	24
Group B3	Aluminum Ammonium Sulfate, 5.0 wt%	120	24	54	30.8	0.57	96	48	48	24	72	24	48	48	120
Group C1	Aluminum Phosphate, 0.001 wt%	72	24	51	20.0	0.39	48	48	48	72	72	24	24	48	72
Group C2	Aluminum Phosphate, 0.5 wt%	96	24	60	22.2	0.37	72	72	96	48	24	72	72	48	48
Group C3	Aluminum Phosphate, 5.0 wt%	144	48	78	33.3	0.43	96	48	72	48	48	96	72	96	144
Group D1	Aluminum Nitrate, 0.001 wt%	72	24	51	15.4	0.30	48	72	48	24	48	48	48	48	72
Group D2	Aluminum Nitrate, 0.5 wt%	72	24	33	17.9	0.54	48	24	24	24	24	24	24	48	72
Group D3	Aluminum Nitrate, 5.0 wt%	48	24	33	12.4	0.38	24	24	24	24	24	24	48	48	48
Group E1	Aluminum Fluoride, 0.001 wt%	72	24	57	17.9	0.31	48	48	24	48	72	48	72	72	72
Group E2	Aluminum Fluoride, 0.5 wt%	48	24	42	11.1	0.26	24	48	48	48	48	48	48	24	24
Group E3	Aluminum Fluoride, 5.0 wt%	48	24	33	12.4	0.38	24	24	48	48	24	48	48	24	24
Group F1	Zn(a)/Pretreat/SP0.5/DRD Control for A-E	72	24	51	20.0	0.39	48	24	24	48	72	48	72	48	72
Group F2	Zn(a)/SP0.5/DRD Only	96	48	66	17.0	0.26	48	72	48	48	72	48	72	96	72
Group F3	Zinc Plate(a) Only Control	24	24	24	0.0	0.00	0	24	24	24	24	24	24	24	24
Group G1	Pretreat/0.001 wt% Al K Sulfate/SP0.5 DRD	72	24	51	15.4	0.30	48	48	48	48	72	24	48	48	72
Group G2	Pretreat/0.5 wt% Al K Sulfate/SP0.5 DRD	96	24	57	22.0	0.39	72	24	72	48	72	48	48	48	96
Group G3	Pretreat/5.0 wt% Al K Sulfate/SP0.5 DRD	72	24	57	17.9	0.31	48	72	72	48	72	24	72	48	48
Group G4	Pretreat/SP0.5/D/5.0 wt% Al K Sulfate/D	48	24	39	12.4	0.32	24	48	48	48	48	48	24	24	24
Group H1	Pretreat/0.001 wt% Al Tartrate/SP0.5 DRD	48	24	39	12.4	0.32	24	48	48	24	48	48	48	24	24
Group H2	Pretreat/0.5 wt% Al Tartrate/SP0.5 DRD	72	24	45	15.4	0.34	48	48	24	48	48	72	48	24	48
Group H3	Pretreat/5.0 wt% Al Tartrate/SP0.5 DRD	48	24	30	11.1	0.37	24	24	24	48	24	24	24	48	24
Group I1	Pretreat/0.001 wt% NaNH4PO4/SP0.5 DRD	48	24	39	12.4	0.32	24	48	48	24	48	48	24	24	48
Group I2	Pretreat/0.5 wt% NaNH4PO4/SP0.5 DRD	72	24	48	18.1	0.38	48	24	48	48	24	48	48	24	24
Group I3	Pretreat/5.0 wt% NaNH4PO4/SP0.5 DRD	72	24	45	15.4	0.34	48	48	48	72	24	24	48	48	48
Group J1	Pretreat/0.001 wt% Na D Gluconate/SP0.5 DRD	72	24	48	12.8	0.27	48	24	48	48	72	48	48	48	48
Group J2	Pretreat/0.5 wt% Na D Gluconate/SP0.5 DRD	72	24	48	18.1	0.38	48	48	24	48	72	24	72	48	48
Group J3	Pretreat/5.0 wt% Na D Gluconate/SP0.5 DRD	96	48	63	17.9	0.28	48	48	96	72	48	72	48	72	48
Group K1	Zn(a)/Pretreat/SP0.5 DRD	96	24	48	22.2	0.46	72	48	48	96	24	24	48	48	48
Group K2	Zn(b)/Pretreat/SP0.5 DRD Control For G-K	96	24	54	21.3	0.39	72	48	48	96	24	48	48	72	48
Group K3	Zn(b)SP 0.5 DRD only	144	48	72	38.5	0.53	96	48	48	48	72	48	120	144	48
Group K4	Zn(b) Zinc Plate Only	24	24	24	0.0	0.00	0	24	24	24	24	24	24	24	24
Group K5	SP 0.5 D/pH 3.4 Acetic Acid/D	72	48	51	8.5	0.17	24	48	48	48	48	48	48	48	72

TABLE 2

ID	Description	Max	Min	Average	Range	St. Dev.	CV	SAMPLE 1	SAMPLE 2	SAMPLE 3	SAMPLE 4	SAMPLE 5	SAMPLE 6	SAMPLE 7	SAMPLE 8
Group A1	Sodium Acetate, 0.001 wt%	168	96	135	72.0	22.0	0.16	120	144	96	120	144	144	168	144
Group A2	Sodium Acetate, 0.5 wt%	168	120	135	48.0	22.0	0.16	120	120	120	168	144	120	168	120
Group A3	Sodium Acetate, 5.0 wt%	168	96	138	72.0	24.8	0.18	96	120	120	168	144	144	144	168
Group B1	Aluminum Ammonium Sulfate, 0.001 wt%	144	96	111	48.0	17.9	0.16	96	96	96	120	120	96	144	120
Group B2	Aluminum Ammonium Sulfate, 0.5 wt%	144	96	114	48.0	17.0	0.15	96	96	120	120	144	120	120	96
Group B3	Aluminum Ammonium Sulfate, 5.0 wt%	144	72	111	72.0	25.5	0.23	72	96	96	120	96	120	144	144
Group C1	Aluminum Phosphate, 0.001 wt%	144	96	126	48.0	21.3	0.17	120	96	144	144	96	144	120	144
Group C2	Aluminum Phosphate, 0.5 wt%	144	120	123	24.0	8.5	0.07	120	120	120	120	120	144	120	120
Group C3	Aluminum Phosphate, 5.0 wt%	168	96	132	72.0	25.7	0.19	96	120	120	120	144	120	168	168
Group D1	Aluminum Nitrate, 0.001 wt%	168	120	135	48.0	17.9	0.13	120	120	120	168	144	120	144	144
Group D2	Aluminum Nitrate, 0.5 wt%	144	96	108	48.0	18.1	0.17	96	96	120	96	96	96	120	144
Group D3	Aluminum Nitrate, 5.0 wt%	144	96	114	48.0	17.0	0.15	96	96	96	120	120	120	120	144
Group E1	Aluminum Fluoride, 0.001 wt%	144	120	123	24.0	8.5	0.07	120	120	120	120	120	120	120	144
Group E2	Aluminum Fluoride, 0.5 wt%	144	96	111	48.0	17.9	0.16	120	120	120	96	96	96	96	144
Group E3	Aluminum Fluoride, 5.0 wt%	120	96	108	24.0	12.8	0.12	96	96	120	120	120	120	96	96
Group F1	Zn(a)/Pretreat/SP0.5/DRD Control for A-E	144	120	129	48.0	12.4	0.10	120	120	120	144	120	144	120	144
Group F2	Zn(a)/SP0.5/DRD Only	168	144	153	24.0	12.4	0.08	144	144	144	144	168	144	168	168
Group F3	Zinc Plate(a) Only Control	72	48	60	24.0	12.8	0.21	48	72	48	72	72	48	48	72
Group G1	Pretreat/0.001 wt% Al K Sulfate/SP0.5 DRD	216	168	192	48.0	12.8	0.07	192	216	192	192	192	168	192	192
Group G2	Pretreat/0.5 wt% Al K Sulfate/SP0.5 DRD	216	168	198	48.0	17.0	0.09	168	192	192	216	216	216	192	192
Group G3	Pretreat/5.0 wt% Al K Sulfate/SP0.5 DRD	240	168	195	72.0	27.0	0.14	240	192	192	216	168	216	168	168
Group G4	Pretreat/SP0.5/0.5 wt% Al K Sulfate/D	216	168	189	48.0	20.0	0.11	168	216	192	192	192	168	168	216
Group H1	Pretreat/0.001 wt% Al Tartrate/SP0.5 DRD	168	96	126	72.0	28.0	0.22	168	144	96	96	144	144	120	96
Group H2	Pretreat/0.5 wt% Al Tartrate/SP0.5 DRD	240	168	189	72.0	23.8	0.13	192	192	168	168	240	192	168	192
Group H3	Pretreat/5.0 wt% Al Tartrate/SP0.5 DRD	216	120	177	96.0	33.8	0.19	168	168	216	144	120	216	192	192
Group I1	Pretreat/0.001 wt% NaH4PO4/SP0.5 DRD	216	144	180	72.0	22.2	0.12	216	192	168	168	192	168	144	192
Group I2	Pretreat/0.5 wt% NaH4PO4/SP0.5 DRD	216	168	198	48.0	17.0	0.09	216	192	192	216	192	216	168	192
Group I3	Pretreat/5.0 wt% NaH4PO4/SP0.5 DRD	192	168	180	24.0	12.8	0.07	192	192	192	168	168	168	168	192
Group J1	Pretreat/0.001 wt% Na D Gluconate/SP0.5 DRD	192	144	165	48.0	20.0	0.12	192	168	144	144	168	144	168	192
Group J2	Pretreat/0.5 wt% Na D Gluconate/SP0.5 DRD	216	168	198	48.0	17.0	0.09	216	192	192	216	192	216	168	192
Group J3	Pretreat/5.0 wt% Na D Gluconate/SP0.5 DRD	264	192	219	72.0	23.8	0.11	192	264	216	216	240	216	216	192
Group K1	Zn(a)/Pretreat/SP0.5 DRD	216	120	156	96.0	28.7	0.18	144	144	216	120	168	168	144	144
Group K2	Zn(b)/Pretreat/SP0.5 DRD Control For G-K	240	192	222	48.0	24.8	0.11	192	240	240	240	240	192	240	192
Group K3	Zn(b)SP 0.5 DRD Only	288	168	219	120.0	39.4	0.18	216	216	192	216	192	264	288	168
Group K4	Zn(b) Zinc Plate Only	144	96	123	48.0	15.4	0.13	120	144	96	144	120	120	120	120
Group K5	SP 0.5 DIPH 3.4 Acetic Acid/D	216	168	201	48.0	17.9	0.09	216	168	216	216	192	216	192	192

[0073] While the apparatus, compositions and methods of this invention have been described herein, it will be apparent to those of skill in the art that variations may be applied to the process described herein without departing from the concept and scope of the invention. All such similar substitutes and modifications apparent to those skilled in the art are deemed to be within the scope and concept of the invention and the appended claims.

[0074] THE FOLLOWING IS CLAIMED:

1. A method for treating a substrate having an electrically conductive surface comprising:

preparing a medium comprising water and at least one silicate and wherein the medium has a basic pH,

passing a current through the medium and then;

contacting at least a portion of the surface with the medium.

2. The method of Claim 1 wherein the medium further comprises colloidal silica, and wherein the medium is substantially free of chromates and VOCs.

3. A method for treating a metallic or an electrically conductive surface comprising:

preparing a medium comprising water and at least one silicate and wherein the medium has a basic pH,

placing an anode and a cathode in electrical contact with the medium,

exposing at least a portion of the surface to a medium,

passing a current through the medium wherein the surface is not in direct contact with the anode or cathode.

4. The method of Claim 3 wherein the colloidal silica has a particle size of less than about 50 nanometers.

5. The method of Claim 1 wherein the surface comprises at least one member selected from the group consisting of copper, nickel, tin, iron, zinc, aluminum, magnesium, stainless steel and steel and alloys thereof.

6. The method of Claim 1 further comprising drying and rinsing and said rinsing comprises contacting the surface with a second medium comprising a combination comprising water and at least one water soluble compound selected from the group

consisting of carbonates, chlorides, fluorides, nitrates, zirconates, titanates, sulphates, water soluble lithium compounds and silanes.

7. The method of Claim 1 wherein the medium comprises at least one dopant selected from the group consisting of zinc, cobalt, molybdenum, nickel and aluminum.

8. The method of Claim 6 wherein said drying is conducted at a temperature of at least about 120C.

9. The method of Claim 5 wherein said surface comprises zinc or zinc alloys.

10. The method of Claim 1 wherein said surface comprises a chromated surface.

11. The method of Claim 3 wherein the surface comprises a chromated surface.

12. The method of Claim 3 wherein said medium further comprises at least one water dispersible polymer.

13. The method of Claim 1 wherein said method further comprises contacting with at least one acid.

14. The method of Claim 9 wherein said surface comprises zinc nickel alloys.

15. The method of Claim 1 further comprising pretreating the surface prior to said contacting.

16. The method of Claim 1 further comprising applying at least one coating selected from the group consisting of latex, silanes, epoxies, silicone, amines, alkyds, urethanes, polyester and acrylics.

17. The method of Claim 15 wherein the pretreating comprises contacting the surface with at least one member selected from the group consisting of sodium acetate, aluminum ammonium sulfate, aluminum phosphate, aluminum nitrate, aluminum fluoride, aluminum potassium sulfate, aluminum tartate, sodium ammonium phosphate and sodium gluconate.

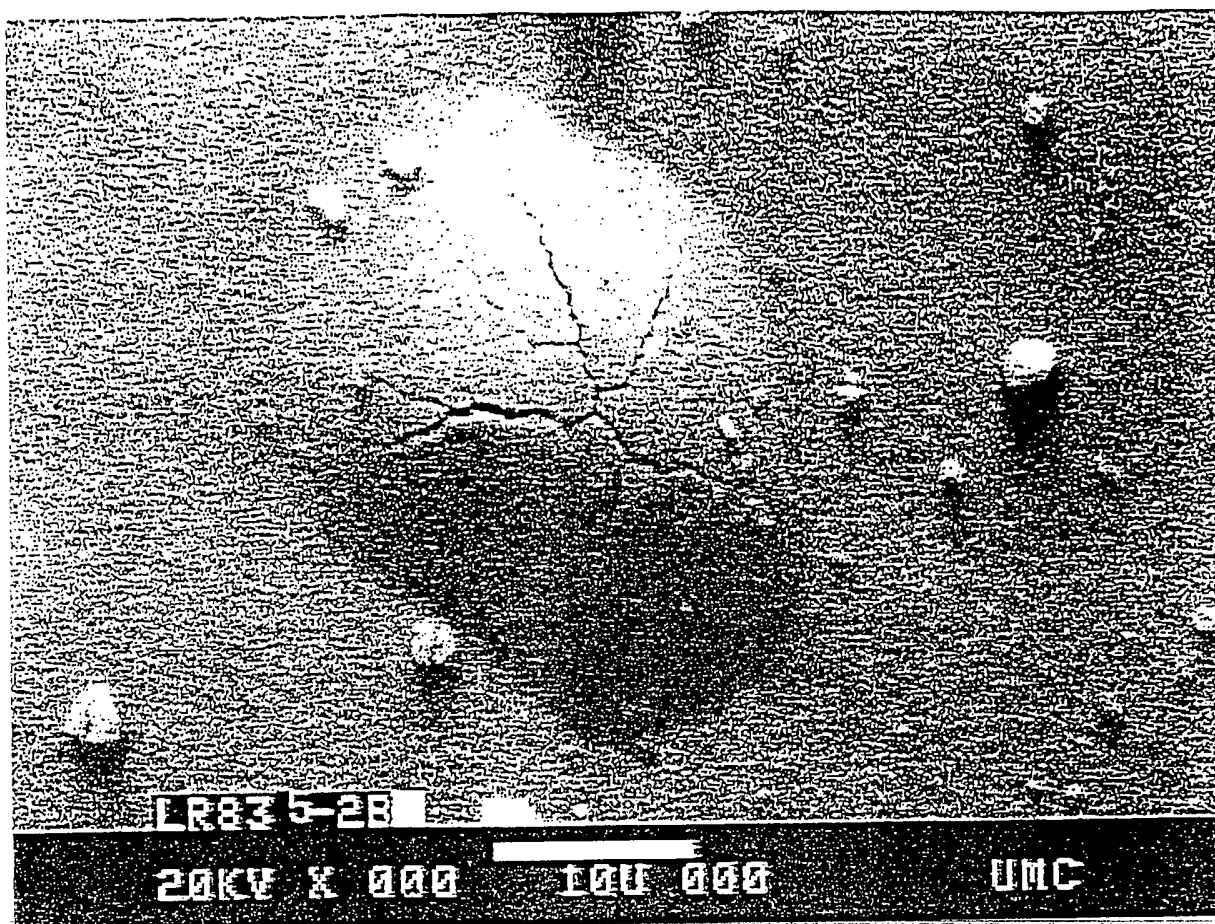
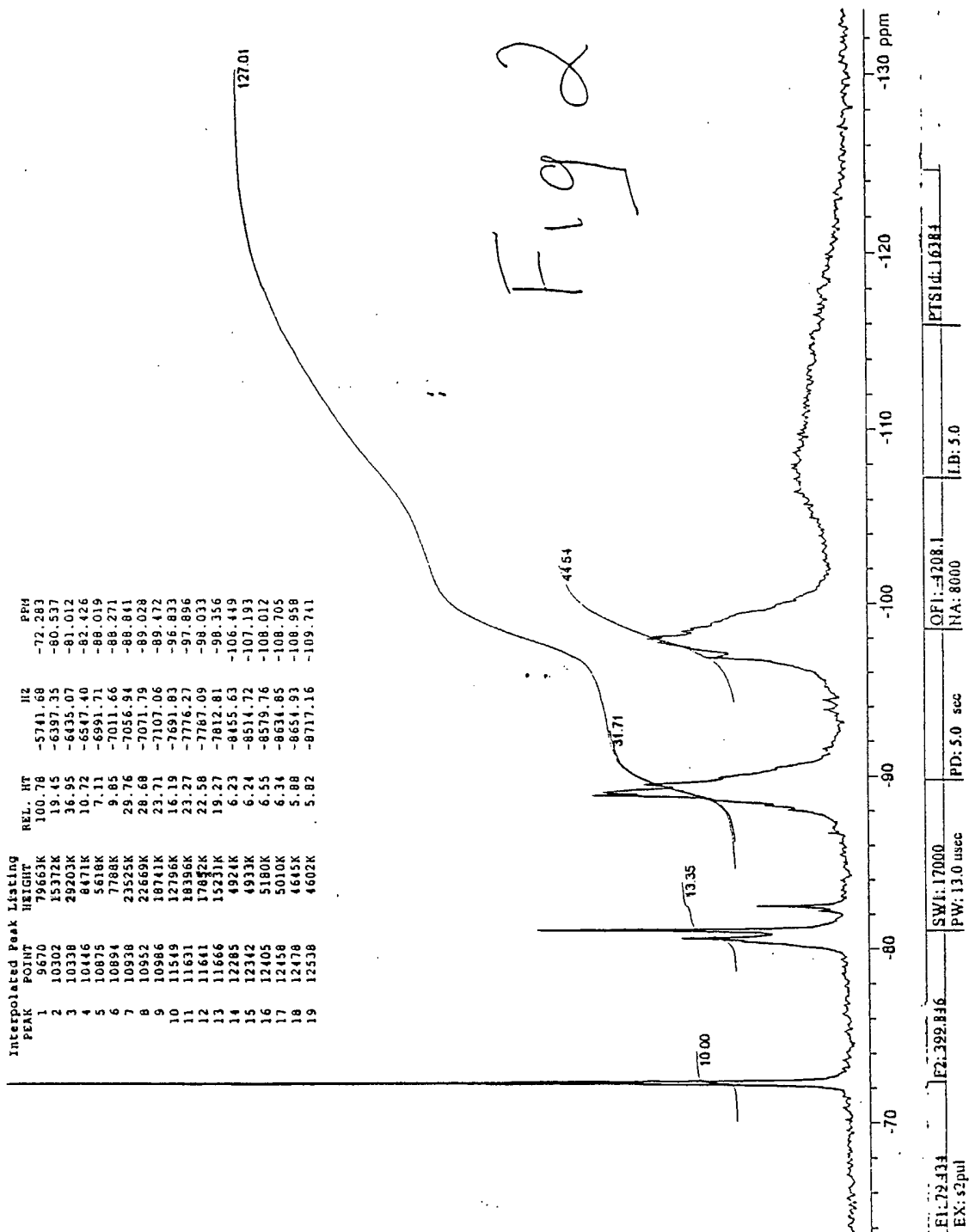


Fig 1

NMR Scans



NMR Scans

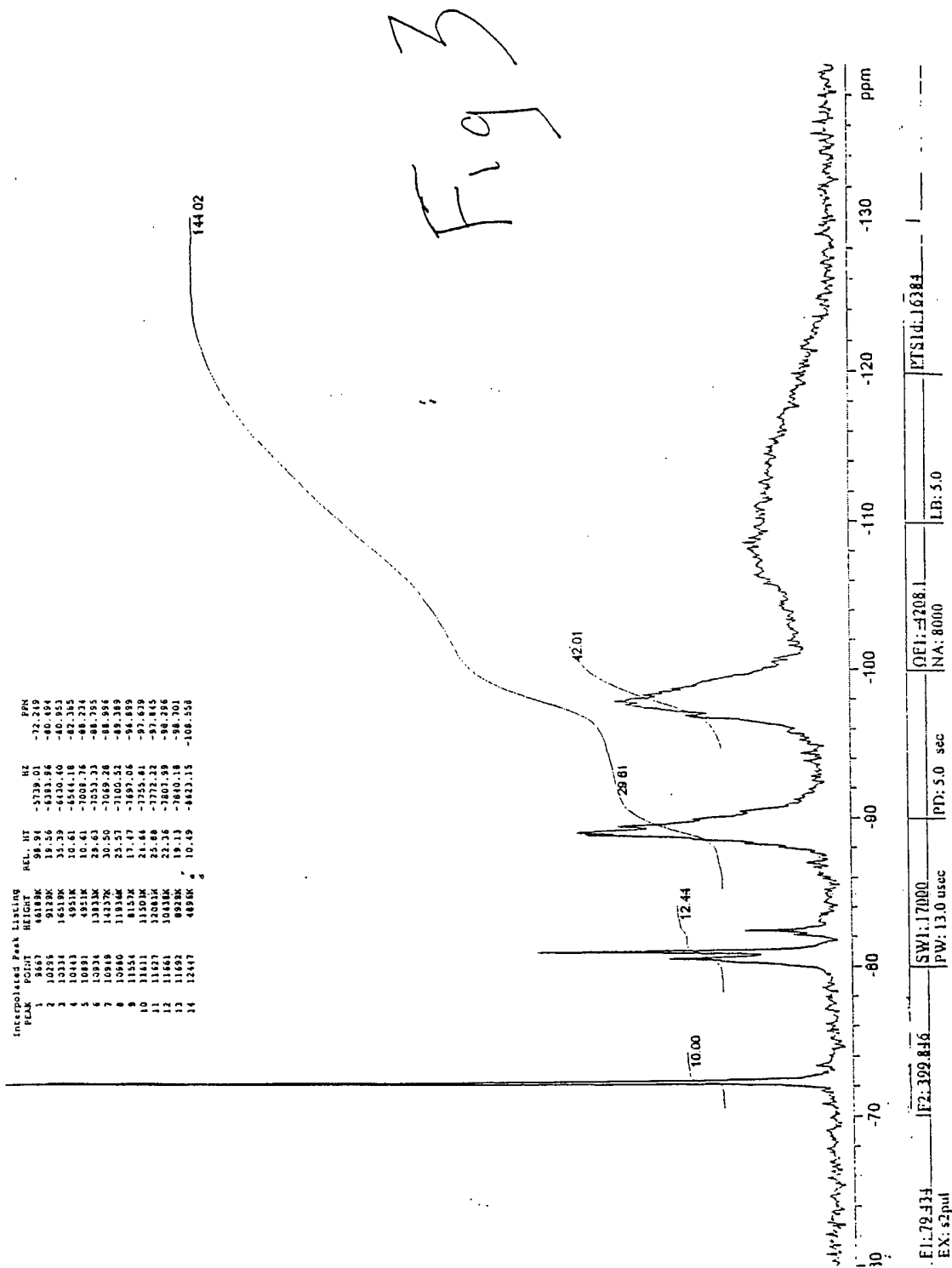


Fig 4

