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# (54) METHOD FOR COATING SUBSTRATE WITH METAL OXIDE COATING

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## (57) ABSTRACT

The method is disclosed for coating or impregnating a substrate with a metal oxide. The method includes the steps of applying a liquid metal carboxylate composition, or a solution thereof, to a substrate material, and exposing the substrate material to an environment that will cause vaporization or dissipation of any excess carboxylic acids in the liquid metal carboxylate composition and conversion of the metal carboxylates to metal oxides.

# METHOD FOR COATING SUBSTRATE WITH METAL OXIDE COATING

## FIELD OF THE INVENTION

**[0001]** The present invention relates generally to the field of surface coatings. In particular, the invention is a method for coating a wide variety of different substrates with a wide variety of metal oxide coatings.

## BACKGROUND OF THE INVENTION

**[0002]** It is desirable in many situations to coat or impregnate the outer surface of a substrate with a coating, including a metal oxide coating.

**[0003]** One method of coating substrates, such as a the ceramic insulator of a sparkplug, using active noble metals, such as silver, palladium or platinum, is disclosed in German Patent 3918272. The primary disadvantage of this method is its high cost. The use of platinum and other noble metals adds significantly to the cost of materials used to form the coating.

**[0004]** One known method for the formation of metal oxide coatings on substrates is via the electrochemical sedimentation of metal oxides from solution. However, this method can only used to coat electrically conductive substrates, a significant limitation where the substrate is nonconductive.

**[0005]** Another method of forming metal oxide coatings on substrates is a sputtering process. In this process, a metal oxide powder is vaporized, using, for example, laser, plasma, flame or detonation methods. The vapors are carried in a gas carrier until they reach the surface to be coated. This surface is generally relatively cool, so that the vaporized metal oxide powder condenses on the surface.

**[0006]** The sputtering process is impractical and expensive to use for coating most substrates, making it commercially unreasonable. It requires the use of specialized manufacturing equipment to maintain the necessary vacuum conditions. These requirements increase the cost and difficulty of manufacturing the coated substrate product. Further, the materials used in the sputtering process, solid solutions of oxides, are expensive.

**[0007]** Detonation spraying is another possible method that could be used to produce coatings on various substrates. However, this method requires a large amount of catalyst material and specialized manufacturing equipment.

**[0008]** Another potential method for coating substrates is by deposition of metal oxides from aqueous solutions, followed by heat treatment. However, this method requires the use of a binder, such as phosphoric acid, in the metal oxide solution. The presence of phosphorus containing compounds in the catalytic layer reduces its catalytic activity.

**[0009]** A further potential method is chemical vapor deposition (CVD) However, CVD requires the use of a carefully developed system of safety equipment, as toxic components are used in this process. These materials include β-diketones and metal-carbonyl complexes.

**[0010]** Another known method for the deposition of a metal oxide coating on a substrate is described in U.S.S.R. Inventors Certificate No. 923232. This process uses a single trivalent metal salt formed by adding the metal to a solution of carboxylic acids. The salt is applied to a substrate and subjected to a temperature of 500 to 600° C. for 20 to 30 seconds in a nonoxidizing atmosphere.

**[0011]** This process suffers from several drawbacks. First, it requires the use of a special furnace that contains a nonoxidizing atmosphere. In addition, the short heat treatment time produces a coating that has internal strains, leading to the lack of a well defined crystalline structure and creating a highly absorptive coating that can absorb water, gases or hydrocarbons. This absorption can make the coating conductive. Furthermore, the use of a single metal in the coating is undesirable because a number of metals, for example zirconium, do not form resistant coatings without additional additives. This would create weak coatings. Finally, this process only uses trivalent and tetravalent metals. As a result, desirable materials, such as nickel, copper and gold, can not be used therein.

**[0012]** As noted above, the above-referenced conventional coating processes suffer from a variety of disadvantages that would make them undesirable for the commercial-scale production of most substrates. In addition, the coatings produced by these methods are relatively thick, which can reduce their adhesion to the substrate and cause scaling or flaking off of the coating. Further, the above methods require additional procedures to remove the coating from areas of the surface where no coating is desired. Finally, all of the above methods have high material consumption, increasing their cost.

## SUMMARY OF THE INVENTION

**[0013]** The present method overcomes the drawbacks described above in known techniques for coating substrates with metal oxides. The method generally comprises the steps of (a) applying a liquid metal carboxylate composition, or a solution thereof, to a substrate material, and (b) exposing the substrate material to an environment that will cause vaporization or dissipation of any excess carboxylic acids in the liquid metal carboxylate composition and conversion of the metal carboxylates to metal oxides.

**[0014]** Usually, step (b) above is carried out by heating the substrate in a furnace, in normal air, at a temperature of at least about 300° C., and preferably of at least about 400° C., for at least about two minutes. However, for some items, such as large cast steel structures, the step can be accomplished by merely exposing the substrate to normal ambient conditions for a sufficiently long time to allow the metal oxide coating to form on the substrate.

**[0015]** The invention also includes devices or structures coated with metal oxide coatings in accordance with the method described above.

**[0016]** Suitable substrates for this process include metals, including steel alloys and aluminum, silica based materials (including optic and fiber optic materials), and various ceramic materials, that need to be protected from a range of environmental conditions, including atmospheres rich in corrosive fluids, combusted or partially combusted hydrocarbons (such as the combustion chambers of internal combustion engines, jet engines, and turbines, and in emission or pollution control systems attached thereto), saline conditions (such as in saline or brine conditioners), lead oxides, abrasive particles or degradative contaminants.

**[0017]** For example, sensors used in catalytic converters, part of the required emission control systems for automobiles manufactured or sold in the United States, are commonly coated with platinum. To reduce the cost of these sensors, the present coating could be used to replace the platinum coating, thereby offering a low-cost alternative. There are numerous other examples of materials that could be coated in accordance with the present invention.

**[0018]** For instance, one embodiment of the present invention is to deposit a metal oxide coating onto various heating elements in heating or air conditioning elements, including condenser or heat exchanger tubes.

**[0019]** Another embodiment of the present invention is to deposit a metal oxide coating onto a casting mold or press mold. For instance, in some countries, press molds for rubber goods, such as tires, gaskets, cups, and seals, are made of hydrocarbon and low alloy steels. The lifetime of these machines can be significantly shortened by corrosion. To increase the life of such products, a thin (up to 5 mcm) metal oxide coating can be applied onto the working surfaces of the press, in accordance with the present method, by heat decomposition of a liquid metal carboxylate composition at, for example, 370-390° C.

**[0020]** Another embodiment of the present invention is to deposit a metal oxide coating onto a metal tool. For instance, formation of a metal oxide coating on the surface of hard-faced (carbide tip) cutting tools will increase the lifetime of cutting tips.

**[0021]** Another embodiment of the present invention is to deposit a metal oxide coating onto salt water marine propellers.

**[0022]** Another embodiment of the present invention is to deposit a metal oxide coating onto turbine blades.

**[0023]** Another embodiment of the present invention is to deposit a metal oxide coating onto metallic moving parts in machinery, such as aluminum parts.

**[0024]** Another embodiment of the present invention is to deposit a metal oxide coating onto steel castings used in air conditioners.

**[0025]** Another embodiment of the present invention is to deposit a metal oxide coating onto silicon or silica based materials, including optic or fiber optic materials.

**[0026]** Another embodiment of the present invention is to deposit a metal oxide coating onto various metal parts exposed to abrasion or continuous high temperatures or high impact conditions (such as tools, dies, stamping materials).

**[0027]** Another embodiment of the present invention is to deposit a metal oxide coating onto boat hulls, for instance, to prevent corrosion and to prevent barnacle formation.

**[0028]** Another embodiment of the present invention is to deposit a metal oxide coating onto molds used for molding nonferrous metals. In the manufacture of such products, a basic mold is first made with a size that is larger than the product to be made, by approximately 50-100 microns. The surface of the mold is then powder coated by a protective coating in such a way that the size of the mold corresponds to the size of the desired article. A primary drawback of this method is the necessity for double treatment of the metal mold, and the restricted resistance of the metal mold. The present invention can be used to form a protective film in the mold when the mold is manufactured, corresponding to the size of the corresponding articles. This involves (1) manufacturing the mold with a size corresponding to the size of the article to be made, and (2) forming a protective surface of approximately 2 microns thickness on the surface of the mold. This provides a significant decrease in labor, and an increase in metal mold resistance at casting of at least 50%.

**[0029]** Another embodiment of the present invention is to deposit an oxide coating of yttrium or cerium on the surface of nichrome heating elements, such as that used in many irons, stoves and resistance furnaces. This will increase the maximum working temperature of a typical nichrome element from approximately 1100° C. to approximately 1220-1250° C. or higher, while increasing the life of the heating element.

**[0030]** While these are examples of various specific applications for the present invention, this list is by no means exhaustive, as the invention can be used to treat a wide variety of different components with a wide variety of different types and combinations of metal oxides.

**[0031]** The term alkyl, as used herein, refer to a saturated straight, branched, or cyclic hydrocarbon, or a combination thereof, typically of $C_1$ to $C_{24}$, and specifically includes methyl, ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl, pentyl, cyclopentyl, isopentyl, neopentyl, hexyl, isohexyl, cyclohexyl, 3-methylpentyl, 2,2-dimethylbutyl, 2,3-dimethylbutyl, heptyl, octyl, nonyl, and decyl.

**[0032]** The terms alkenyl and alkynyl, as used herein, refers to a $C_2$ to $C_{24}$ straight or branched hydrocarbon with at least one double or triple bond, respectively.

**[0033]** The term aryl or aromatic, as used herein, refers to phenyl, naphthyl, or substituted phenyl or naphthyl, wherein the substituent is alkyl, alkenyl, alkynyl or alkoxy.

**[0034]** The liquid metal carboxylate composition is a solution of the carboxylic acid salts of one or more metals ("metal carboxylate"). Metal carboxylates are well known and can be produced by a variety of methods known to one skilled in the art. Non-limiting examples of methods for producing the metal carboxylate are shown in the following reaction schemes:

**[0035]** $RCOOH+Me \rightarrow (RCOO)_nMe^{n+}0.5nH_2$ (for alkaline earth metals, alkali earth metals and thallium);

**[0036]** $RCOOH+Me^{n+}(OH)_n \rightarrow (RCOO)_nMe^{n+}H_2O$ (for practically all metals having a solid hydroxide);

**[0037]** $RCOOH+Me^{n+}(CO_3)_{0.5n} \rightarrow (RCOO)_nMe^{n+} H_2O\ CO_2$ (for alkaline earth metals, alkali earth metals and thalluim); and

**[0038]** $RCOOH+Me^{n+}(X)_n \rightarrow (RCOO)_nMe^{n+}H_mX$ (liquid extraction, usable for practically all metals having solid salts).

**[0039]** The liquid metal carboxylate composition can contain a single metal, to form a single metal carboxylate, or a mixture of metals, to form a corresponding mixture of metal carboxylates. Preferably, the liquid metal carboxylate composition contains a mixture of metals, as these compositions form mixed oxides having superior properties.

[**0040**] Preferably, the solvent used in the liquid metal carboxylate composition is an excess of a liquid carboxylic acid which was used to form the metal carboxylate. Alternatively, the solvent can be the solution of a carboxylic acid in another solvent, including, but not limited to, organic solvents such as acetone, ethanol, methanol, propanol, benzene, toluene, chloroform and dichloromethane.

[**0041**] Carboxylic acids that are suitable for use to form the liquid metal carboxylate composition are those which: (1) can form a metal carboxylate, where the metal carboxylate is soluble in excess acid or another solvent; and (2) can be vaporized at a temperature which overlaps the oxide conversion temperature.

[**0042**] The carboxylic acid should have a formula R-COOH, where R is alkyl, alkenyl, alkynyl or aryl.

[**0043**] Preferably, the liquid monocarboxylic acid comprises one or more carboxylic acids having the formula I below:

$$R\text{—}C(R'')(R')\text{—}COOH \qquad (I)$$

[**0044**] wherein:

[**0045**] R is selected from H and $C_1$ to $C_{24}$ alkyl groups; and

[**0046**] R' and R" are each independently selected from $C_1$ to $C_{24}$ alkyl groups.

[**0047**] Preferably, these alpha branched carboxylic acids have a molecular weight in the range 130 to 420. More preferably, the carboxylic acids have a molecular weight in the range 220 to 270.

[**0048**] Either a single carboxylic acid or a mixture of carboxylic acids can be used to form the liquid metal carboxylate. Preferably, a mixture of carboxylic acids is used. The use of a mixture provides several advantages. First, the mixture has a broader evaporation temperature range, making it more likely that the evaporation temperature of the acid mixture will overlap the metal carboxylate decomposition temperature, allowing the formation of an optimum oxide coating. Second, the production of purified individual acids is expensive. Thus, the use of an individual acid could unnecessarily raise the cost of this method.

[**0049**] The carboxylic acid may be a mixture of tertiary and quaternary carboxylic acids of formula I. One preferred carboxylic acid mixture is a mixture manufactured by the Sterlitamakski Production Complex "KAUSTIK," Bashkortostan, Sterlitamak City, Russia and other petrochemical enterprises, such as the Dneprodzerzhinski Complex in Dneprodzerzhinsk city, Ukraine. These materials are sold under the name "VIK acids." The VIK acids are a material consisting of a mixture of carboxylic acids having the general formula $CH_3(CH_2)_nC(CH_3)(C_2H_5)\text{—}COOH$, wherein n is 7 to 10. The average molecular weight of the acids contained in this mixture is from about 220 to 270. This mixture also contains the acid $CH_3CH_2CH_2CH(CH_3)\text{—}COOH$ as its lowest boiling acid constituent.

[**0050**] The VIK acids should have the properties set forth in Table 1.

TABLE 1

| CHARACTERISTIC | NORM |
|---|---|
| appearance | transparent homogeneous liquid color less or low-yellow. |
| Color, maximum | 7.0 |
| Density at 20 C. g/cm$^3$ | 0.90–0.93 |
| Acid Fraction composition: | |
| content of $C_3$ acids-maximum | 1.0 |
| b) content of $C_5$–$C_{11}$, acids and higher-maximum | 90.0% |
| Acid number, mg KOH/gr | 300–350 |
| Ether number, mg KOH/gr-maximum | 20.0 |
| Water content-maximum | 0.5% |
| Refraction coefficient, $\eta$ 20 C. | 1.42–1.43 |
| 189779.1 | |

[**0051**] The critical properties of the VIK acid are the acid number, which should not be above 380 mg/g KOH and the appearance; the liquid should be clear. The liquid alpha-branched carboxylic acids can be used as received from the manufacturer and do not require any additional purification, such as the removal of alcohol, ethers or other organic impurities.

[**0052**] Metals that are particularly suitable for use to form the liquid metal carboxylates include those selected from the group consisting of: Lithium, Beryllium, Sodium, Magnesium, Potassium, Calcium, Scandium, Titanium, Chromium, Manganese, Iron, Nickel, Cobalt, Copper, Zinc, Gallium, Rubidium, Strontium, Yttrium, Zirconium, Silver, Cadmium, Tin, Cesium, Cerium, Barium, Platinum, Lanthanum, Hafnium, Vanadium, Niobium, Molybdenum, Indium, Promethium, Plutonium, Curium, Californium, Tantalum, Gold, Thallium, Lead, Bismuth, Cerium, Praseodymium, Neodymium, Samarium, Europium, Gadolinium, Terbium, Dysprosium, Holmium, Erbium, Thulium, Ytterbium, Lutetium, Thorium and Plutonium and Uranium.

[**0053**] Any of the above metals or combinations thereof can be used to form coatings according to the present process. Depending on the particular use of the coating, those skilled in the art can select appropriate metal mixtures to form the desired metal or metal oxide coating. For example, the metals can be selected taking into consideration the nature of the substrate to be coated, the purpose of the substrate, and the environment to which the substrate is exposed.

[**0054**] For example, the above-named inventor is filing contemporaneously herewith an application directed to a method for coating the ceramic insulators of sparkplugs, just one of the many applications of the present invention. By way of example, for the formation of a coating on the ceramic insulator of a sparkplug, the oxide coating should not be electrically conductive. In addition, if the engine is operating with a highly enriched fuel mixture, the partial reduction of iron, nickel and cobalt oxides is possible due to the interaction of these oxides with partially combusted fuel products. Thus, in these conditions, the amounts of these materials should be limited to that necessary to provide a stable coating. Preferably in these circumstances, thermodynamically stable oxides, such as chromium and cerium oxides should be the major components of the coating. Similarly, chromium oxide should not be the sole component of the coating for a sparkplug, as it may form agglomerates or a crystalline structure with reduced resistance. Thus, if chromium is used, it is preferably used in combination with other oxides, such as cerium. In addition, the use of divalent nickel with trivalent metals, such as cobalt, iron or chromium, may cause the formation of electrically conductive spinels. The electrically conductive spinels are, of course, undesirable for use on sparkplug insulators, although they may have other applications. Accordingly, if sparkplugs are being coated, the use of nickel with trivalent metals should be carefully monitored.

**[0055]** In general, the liquid metal carboxylate composition preferably contains a mixture of metal carboxylates. This mixture preferably contains one metal carboxylate as its major component and one or more additional metal carboxylates as stabilizing additives. The stabilizing additives are preferably trivalent metal carboxylates. Preferred trivalent stabilizing additives include chromium, iron, manganese and nickel carboxylates. Preferably, the liquid metal carboxylate composition contains both cerium and chromium carboxylates.

**[0056]** For most components in general, the metal forming the metal carboxylate which is the major component of the liquid metal carboxylate composition is preferably present in an amount from about 65 to 97% by weight, relative to the total weight of the metal in the composition. Preferably, the metal forming the metal carboxylate which is the major component is present in an amount from about 80-87% by weight. Another preferred amount for the metal forming the major component of the metal carboxylate composition is in the range from about 90-97% by weight.

**[0057]** The stabilizing additives should be present, such that the total amount of the metal in metal carboxylates which are the stabilizing additives is at least 3% by weight, relative to the total weight of the metal in the liquid metal carboxylate composition. This can be achieved by using 3% of a single stabilizing additive, or less than 3% of more than one stabilizing additive, provided that the total weight of the metal in the stabilizing additives is greater than 3%. Preferably, the total weight of the metal in the stabilizing additives is in a range from about 3% to about 35% by weight. Another preferred total weight range for the metal in the stabilizing additives is from about 3 to 30% by weight. One preferred total weight range for the metal in the stabilizing additives is from about 3 to 10 percent by weight.

**[0058]** Non-limiting examples of liquid metal carboxylate compositions suitable for use in the present process are set forth below. In these compositions, weight range percentages for the metals are based on 100 percent total by weight of the metal in the liquid metal carboxylate composition. As noted above, the minimum amount of the stabilizing additives, those defined below as being present in "up to" a certain amount, is a total stabilizing additive weight of at least 3 percent. For example, the liquid metal carboxylate composition can have 3% of a single stabilizing additive or 1.5% of one stabilizing additives and 1.5% of another, or 2% of one stabilizing additive and 1% of the other. Non-limiting examples of suitable compositions are, particularly preferred in coating sparkplugs, are: up to 15% cobalt, up to 20% nickel, and the balance iron; up to 10% chromium, up to 20% cobalt, and the balance cerium; 3 through 5% cobalt, up to 20% chromium, and the balance cerium.

**[0059]** The amount of metal in the liquid metal carboxylate composition should be enough to provide an adequate metal oxide coating. Preferably, this amount is in the range from about 20 to 150 grams of metal per kilogram of liquid metal carboxylate composition. A preferred amount of metal in the liquid metal carboxylate composition is 30 to 100 grams of metal per kilogram of liquid metal carboxylate composition. More preferably, the liquid metal carboxylate composition contains about 40-60 grams of metal per kg of composition.

**[0060]** Amounts of metal less than 20 grams per kg of composition can be used. However, this low concentration requires that the process be repeated several times to provide an adequate coating.

**[0061]** Similarly, amounts of metal greater than 150 grams per kg of composition can be used, however, the use of more metal raises the cost of the present Method.

**[0062]** One preferred liquid metal carboxylate composition comprises VIK acids and the following metals (metal weight percentages are given relative to the total weight of metal in the liquid metal carboxylate composition):

| | | |
|---|---|---|
| cerium | - | 94 to 96% |
| chromium | - | 2 to 3% |
| Iron | - | 2 to 3% |

**[0063]** The above metals are preferably present in the liquid metal carboxylate composition in an amount from about 30 to 40 grams of metal per kilogram of liquid metal carboxylate composition.

**[0064]** Another preferred liquid metal carboxylate composition comprises VIK acids and the following metals (metal weight percentages are given relative to the total weight of metal in the liquid metal carboxylate composition):

| | | |
|---|---|---|
| Cerium | - | 90% |
| Chromium | - | 7% |
| Cobalt | - | 3% |

**[0065]** The above metals are preferably present in the liquid metal carboxylate composition in an amount of 50 g of metal per kilogram of liquid metal carboxylate composition.

**[0066]** These liquid metal carboxylate compositions are commercially available from the state enterprise Vserossiiski Scientific Research Institute of Chemical Technologies, Moscow, Russia.

**[0067]** As discussed above, the primary purpose of the disclosed method is the production of a metal oxide coating on the surface of a substrate. The method can be carried out on a variety of different structural products or components, whenever it is desirable to provide a metal oxide coating on the product or component. The coating can be applied to individual components prior to assembly into a multicomponent product, or can be applied to a finished multicomponent product.

**[0068]** The liquid metal carboxylate composition can be applied to the substrate neat (without the use of an additional solvent) or in solution. Preferably, the liquid metal carboxylate composition is applied without a solvent.

**[0069]** Any known method of application of the liquid metal carboxylate composition is suitable for use in the present process, so long as it provides an adequate coating of the liquid metal carboxylate composition on the substrate. For example, the substrate component can be dipped into a container of the liquid metal carboxylate composition. Alternatively, a swab, sponge, dropper, pipet or other applicator can be used to apply the liquid metal carboxylate composition to the substrate.

**[0070]** The liquid metal carboxylate composition should be applied at a temperature less than 500 C. Preferably, the liquid metal carboxylate composition is applied to the substrate component at room temperature.

**[0071]** Following application of the liquid metal carboxylate composition to the substrate, the component is exposed to an environment sufficient to vaporize or dissipate excess carboxylic acid in the liquid metal carboxylate composition and to convert the metal carboxylates to metal oxides. The temperature for the treatment should be selected such that the temperature ranges for the evaporation of the carboxylic acid and the formation of the metal oxide overlap, and the temperature should not damage the component onto which the coating is being applied.

**[0072]** For sparkplugs and similar types of components, this temperature is preferably greater than about 400° C. The upper limit for the heat treatment is dependent on the materials contained in the component being treated. The temperature should be selected so that it will not damage the component which is being coated. A preferred temperature range for most ceramic and metal components is from about 400 to 650° C. Another preferred temperature range is from about 400 to 550° C.

**[0073]** During the exposure step of the process, two processes take place. These processes can occur at different temperature levels. The first process is the evaporation or decomposition of the excess carboxylic acid in the liquid metal carboxylate composition. This forms a metal carboxylate layer on the surface of the component. The second stage is the decomposition of the metal carboxylate layer to a metal oxide layer and fixation of that layer on the backing or substrate surface.

**[0074]** To create an oxide layer which is fixed to the substrate surface, it is preferred that there be an interaction between the substrate and the coating during the coating process. Optimum oxide layer production occurs when the temperature at which the carboxylate decomposes and the acid evaporates overlap. That is, when the carboxylate decomposition stage commences, the removal and decomposition of the acid is not complete. Complete removal of the acid, prior to the commencement of carboxylate decomposition can reduce the adhesion of the oxide coating to the substrate.

**[0075]** Without wishing to be bound to any particular mechanism, it is believed that the following process occurs during the So production of the oxide coating. At high temperatures, it is believed that the carboxylic acid etches or otherwise interacts with the substrate, activating it. This allows interaction between the metal carboxylate and the activated substrate, resulting in the formation of a strong substrate-oxide link.

**[0076]** The heating can be conducted either by placing the coated component onto a rack or support and then into a furnace, which has been preheated to a desired temperature, or by placing the coated component into a furnace, followed by heating the furnace to the desired temperature. Any conventional furnace can be used, as no special heating equipment is required, provided, of course, that the furnace will accommodate the size and shape of the component being treated.

**[0077]** In general, the component should be heated for a time adequate to produce a uniform oxide coating. For a furnace which has been preheated to a temperature above 400° C., a preferred minimum time is at least about 2 min. If several different components are being treated simultaneously, uneven heating might take place. For example, the peripheral components will probably heat to working temperature faster than the components located in the center of the group. Accordingly, batches of components should be heated longer, depending on the type of furnace used and the nature of the components.

**[0078]** Preferably, the heat treatment should be carried out for at least two minutes at the desired temperature. More preferably, the heat treatment should be carried out for 15 to 20 minutes.

**[0079]** Following treatment, the component should be allowed to cool to room temperature. Forced air cooling may be used to accelerate the cooling process. The component should not be cooled by treating it with a liquid coolant, as this could damage the coating or the component.

**[0080]** As noted above, while active heating to high temperatures is the preferred method of curing the coating, the exposure step can also be carried out in some situations by exposing the substrate to ambient air conditions for sufficient time to fix the metal oxide coating to the substrate.

**[0081]** The present process is carried out in a normal, i.e. ambient atmosphere. Accordingly, there is no need to provide any special atmosphere in the furnace during the heating process. However, should it be desired, the present process can also be conducted in specialized atmospheres. If a specialized atmosphere is used, it is preferably an oxidizing atmosphere, that is, one which is enriched with oxygen.

**[0082]** As noted above, one particular application of the present invention is for coating sparkplugs. Sparkplugs in internal combustion engines, and igniters in gas turbines and jet engines, are used for igniting combustible mixtures of gases and vapors.

**[0083]** Typically, sparkplugs used in internal combustion engines include a ceramic insulator, which surrounds a central electrode. The end portion of the sparkplug, including the end of the ceramic insulator, is exposed to the interior of the combustion chamber of the engine. During normal operation of the engine, there are times when operating conditions contaminate the ceramic insulator of the sparkplug. Often, this contamination takes the form of electroconducting coke. This contamination can occur, for example, during engine idle when the engine has just been started and the fuel mixture is enriched, when the weather is cold, and when the engine is not properly tuned. It has been found that even when an engine is properly tuned, carbonization of the sparkplug can still take place, for example, when driving on a cold engine or using an enriched fuel mixture. The contamination can also take the form of lead-oxide, due to the presence of lead in leaded gasolines.

**[0084]** The contamination of the sparkplug's ceramic insulator can interfere with the operation of the sparkplug. For example, contamination with electroconductive coke or lead oxide reduces the sparking ability of the sparkplug, because the electrical current dissipates through the contaminant layer to the metal casing of the sparkplug.

**[0085]** The present invention prevents or inhibits contamination of the sparkplug's ceramic insulator by carbon-based materials, such as coke, or by lead-oxide. The method can be used either during the sparkplug manufacturing process, for example, on an intermediate assembly, such as the ceramic insulator, or on the completed sparkplug. The present coating process can be used with any known process for manufacturing sparkplugs. For example, the present oxide coating can be applied to the sparkplug's ceramic insulator prior to its assembly into the completed sparkplug. Alternatively, the coating can be applied to an assembled sparkplug. In addition, the present process can be used to form oxide coatings on sparkplugs which have been used in internal combustion engines, provided that the used sparkplug has been cleaned of any contaminants prior to formation of the oxide coating.

## EXAMPLES

**[0086]** The following examples illustrate the application of the present process to the coating of sparkplugs.

**[0087]** The metal carboxylate compositions used in Examples 1 to 3 were obtained from VserosBiiski Scientific Research Institute of Chemical Technologies, in Moscow, Russia.

### Example 1 Preparation of Coated Insulator

**[0088]** The upper electrode to which a sparkplug wire was attached, was removed from a group of sparkplugs. The sparkplugs were then placed in a basket in a container over a boiling hydrocarbon solvent, in order to remove any grease or organic contamination which was present on the sparkplug. The basket containing the sparkplugs was removed from the degreasing chamber and was cooled to a temperature below 50° C.

**[0089]** The degreased sparkplugs were placed in a holder, with the threaded portion of the sparkplug facing up, and were placed in a furnace which had been preheated to a temperature in the range 180 to 220° C. This treatment removed any solvent or moisture which had been absorbed onto the sparkplug. The sparkplugs were removed from the furnace and cooled to a temperature below 50° C.

**[0090]** Two drops of a liquid metal carboxylate mixture were manually applied to the tip of the central electrode insulator of each spark plug. The metal carboxylate mixture had the following proportions of metal: 90% cerium, 7% chromium, and 3% cobalt. The carboxylic acid was VIK acid. The total metal concentration in the liquid carboxylate mixture was 50 g metal per kilogram of liquid carboxylate mixture.

**[0091]** The sparkplugs were placed in a furnace which had been heated to a temperature of 420° C. and were kept in the furnace for 30 minutes, forming the oxide coating. At the conclusion of the heat treatment, the sparkplugs were cooled to room temperature, and the upper electrode was reassembled into the sparkplug to provide the completed article.

### Example 2 Preparation of Coated Sparkplug

**[0092]** A Russian type All/1 sparkplug was prepared (degreased and dried) as set forth in Example 1, without the removal of the central electrode. The sparkplugs central insulator was dipped into the liquid carboxylate composition used in Example 1 to a depth between 10 to 15 mm. The sparkplug was then introduced into a furnace which had been preheated to 650° C., kept in the furnace for 10 minutes, removed and cooled to room temperature.

### Example 3 Coating of a Previously used Sparkplug

**[0093]** The procedure of Example 2 was repeated using a Russian All/l sparkplug which had been used in an internal combustion engine which had been run for 20,000 kilometers. A coated sparkplug was produced.

### Example 4 use of Coated Sparkplug

**[0094]** The sparkplugs manufactured according to the process set forth in Example 2 were used in a Lada automobile to determine their effects on the performance of the automobile, compared to uncoated sparkplugs. The use of the sparkplugs coated according to the present process significantly reduced the average time necessary to start the engine of a Lada automobile in cold weather from 2 min to 15-20 sec. In addition, the fuel consumption economy of the engine was improved by 5-7%.

**[0095]** As noted above, the present method can be used to coat numerous different substrates, with a variety of metal oxides. While the invention has been described by reference to various specific examples, it should be understood that the invention is not limited to those specific examples, and various modifications may be made to the embodiments described above without departing from the scope and spirite of the invention as claimed below.

What is claimed is:

**1**. A method for forming a metal oxide coating on a substrate, comprising the steps of:

(a) applying metal carboxylate composition, or a solution thereof, to a substrate material, and

(b) exposing the substrate material to an environment that will cause vaporization or dissipation of any excess carboxylic acids in the liquid metal carboxylate composition and conversion of the metal carboxylates to metal oxides.

**2**. The method or claim 1, wherein the liquid metal carboxylate composition comprises a solution of the metal salt of a carboxylic acid.

**3**. The method of claim 2, wherein the carboxylic acid is an alpha-branched carboxylic acid having having the formula

R—C(R")(R')—COOH

wherein:

R is selected from H and $C_1$ to $C_{24}$ alkyl groups; and

R' and R" are each independently selected from $C_1$ to $C_{24}$ alkyl groups.

**4**. The method of claim 2, wherein the carboxylic acid is a mixture of carboxylic acids having the formula $CH_3(CH_2)_nC(CH_3)(C_2H_5)$—COOH, wherein n is 7 to 10.

**5**. The method of claim 4, wherein the average molecular weight of the acids contained in this mixture is from about 220 to 270.

**6**. The method of claim 5, wherein the mixture of carboxylic acids contains the acid $CH_3CH_2CH_2CH(CH_3)$—COOH as its lowest boiling acid constituent.

**7**. The method of claim 2, wherein the liquid metal carboxylate composition comprises a mixture of metals.

**8**. The method of claim 2, wherein the liquid metal carboxylate composition comprises one or more metals selected from the group consisting of Lithium, Beryllium, Sodium, Magnesium, Potassium, Calcium, Scandium, Titanium, Chromium, Manganese, Iron, Nickel, Cobalt, Copper, Zinc, Gallium, Rubidium, Strontium, Yttrium, Zirconium, Silver, Cadmium, Tin, Cesium, Cerium, Barium, Lanthanum, Hafnium, Tantalum, Gold, Thallium, Lead, Bismuth, Cerium, Praseodymium, Neodymium, Samarium, Europium, Gadolinium, Terbium, Dysprosium, Holmium, Erbium, Thulium, Ytterbium, Lutetium, Thorium and Uranium.

**9**. The method of claim 3, wherein the liquid metal carboxylate composition comprises one or more metals selected from the group consisting of Lithium, Beryllium, Sodium, Magnesium, Potassium, Calcium, Scandium, Titanium, Chromium, Manganese, Iron, Nickel, Cobalt, Copper, Zinc, Gallium, Rubidium, Strontium, Yttrium, Zirconium, Silver, Cadmium, Tin, Cesium, Cerium, Barium, Lanthanum, Hafnium, Tantalum, Gold, Thallium, Lead, Bismuth, Cerium, Praseodymium, Neodymium, Samarium, Europium, Gadolinium, Terbium, Dysprosium, Holmium, Erbium, Thulium, Ytterbium, Lutetium, Thorium and Uranium.

**10**. The method of claim 4, wherein the liquid metal carboxylate composition comprises one or more metals selected from the group consisting of Lithium, Beryllium, Sodium, Magnesium, Potassium, Calcium, Scandium, Titanium, Chromium, Manganese, Iron, Nickel, Cobalt, Copper, Zinc, Gallium, Rubidium, Strontium, Yttrium, Zirconium, Silver, Cadmium, Tin, Cesium, Cerium, Barium, Lanthanum, Hafnium, Tantalum, Gold, Thallium, Lead, Bismuth, Cerium, Praseodymium, Neodymium, Samarium, Europium, Gadolinium, Terbium, Dysprosium, Holmium, Erbium, Thulium, Ytterbium, Lutetium, Thorium and Uranium.

**11**. The method of claim 2, wherein the metal is a mixture comprising:

up to 15% by weight of cobalt;

up to 20% by weight of nickel; and

the balance iron;

wherein the minimum total amount of cobalt and nickel is at least 3%.

**12**. The method of claim 2, wherein the metal is a mixture comprising:

up to 20% by weight of cobalt;

up to 10% by weight of chromium; and

the balance cerium;

wherein the minimum total amount of cobalt and chromium is at least 3%.

**13**. The method of claim 2, wherein the metal is a mixture comprising:

3 through 5% by weight of cobalt,

0 through 20% by weight of chromium,

and the balance cerium.

**14**. The method of claim 1 wherein the vaporization or dissipation of any excess carboxylic acids in the liquid metal carboxylate composition and conversion of the metal carboxylates to metal oxides is carried out by heating the coated substrate.

**15**. The method of claim 14, wherein the substrate is heated to a temperature greater than about 400° C.

**16**. The method of claim 2, wherein the amount of metal in the liquid metal carboxylate composition is preferably in the range of 30-50 grams of metal per kilogram of liquid metal carboxylate composition.

**17**. The method of claim 2, wherein the amount of metal in the liquid metal carboxylate composition is 30 to 40 grams of metal per kilogram of liquid metal carboxylate composition.

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