

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
14 June 2007 (14.06.2007)

PCT

(10) International Publication Number
WO 2007/067972 A1

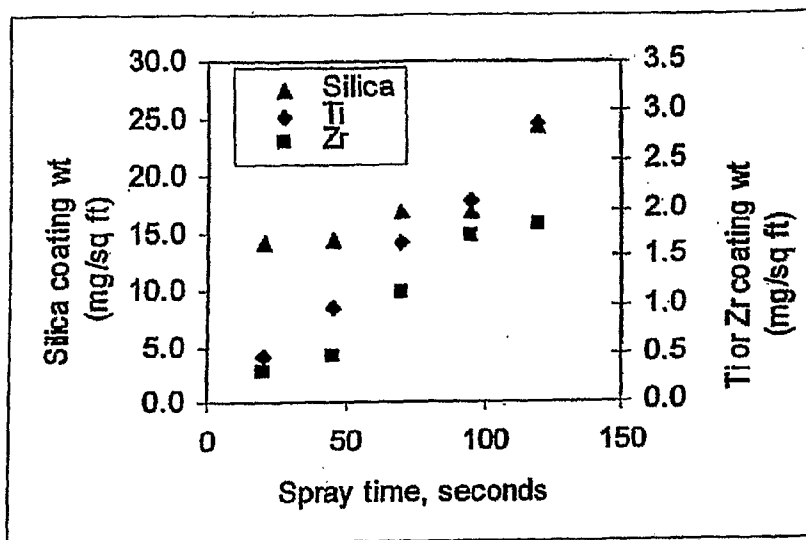
- (51) International Patent Classification:
C23C 22/00 (2006.01)
- (21) International Application Number:
PCT/US2006/061781
- (22) International Filing Date:
8 December 2006 (08.12.2006)
- (25) Filing Language:
English
- (26) Publication Language:
English
- (30) Priority Data:
11/296,259 8 December 2005 (08.12.2005) US
- (71) Applicant (for all designated States except US): **HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN** [DE/DE]; Henkelstrasse 67, 40589 Duesseldorf (DE).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **KOLBERG, Keith, V.** [US/US]; 2880 Veronica Drive, St. Joseph, MI 49085 (US). **KIRSCH, Gabriel** [US/US]; 38515 Capetown Court, Clinton Township, MI 48038 (US).
- (74) Agent: **CAMERON, Mary, K.**; Henkel of America, INC., Patent Department, Suite 200, 2200 Renaissance Boulevard, Gulph Mills, PA 19406 (US).

- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

- Published:**
- with international search report
 - before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PROCESS OF COATING METALS PRIOR TO COLD FORMING



(57) Abstract: A process of forming on a metal substrate a composition prior to the substrate being cold worked. The process includes a step of contacting the substrate with an aqueous composition comprising acid-stable particles and one or more fluoroacids. The amount of the acid-stable particles in the coating composition is from 0.005% to 8% by weight on a dry weight basis.

WO 2007/067972 A1

PROCESS OF COATING METALS PRIOR TO COLD FORMING

Field of the Invention

[0001] The present invention relates to a process for cold forming metals, the process utilizing coating compositions, in particular, coating compositions comprising acid-stable silica particles, that can be applied to the metals prior to cold forming.

Background of the Invention

[0002] A coating is often applied to metal substrates, especially metal substrates that contain iron such as steel, prior to the application of a protective or decorative coating. The coating minimizes the amount of corrosion to the metal substrate, if and when, the metal substrate is exposed to moisture and oxygen. Many of the present coating compositions are based on metal phosphates, and rely on a chrome-containing rinse. The metal phosphates and chrome rinse solutions produce waste streams that are detrimental to the environment. As a result, there is the ever-increasing cost associated with their disposal.

[0003] Coating compositions can be applied without chrome rinse solutions. For example, U.S. Patent 3,966,502 discloses post-treating phosphated metals with zirconium-containing rinse solutions. However, this application process is only suitable for use over a limited number of metal substrates, and the generation of metal phosphate waste streams is not alleviated.

[0004] U.S. Patent No. 5,534,082 to Dollman et al. and U. S. Patent Nos. 5,281,282 and 5,356,490 to Dolan et al. describe non-chrome coating compositions containing a fluoroacid such as fluorotitanic acid, silica, and a water-soluble polymer such as an acrylic acid polymer and/or a polymer with hydroxyl functionality. By heating the silica and fluoroacid, the silica is dissolved, or at least partially dissolved, until the solution is clear. As a result, the silica particles used in these coating compositions are not acid-stable particles.

[0005] The pH of these compositions is very acidic, and ranges from 0 to 4, preferably from 0 to 1. The coatings compositions enhance the corrosion resistance of steel and galvanized steel substrates.

[0006] U.S. Patent No. 5,938,861 to Inoue et al. describes forming a coating on metal substrates, except aluminum. The coating composition includes an oxidative compound such as nitric acid or hydrogen peroxide, silicate or silicon dioxide particles, and a metal cation, oxymetal anion, or fluorometallate anion of Ti, Zr, Ce, Sr, V, W, and Mo.

[0007] EP 1130131A2 to Toshiaki et al. describes a non-chrome coating composition that contains a metallic surface-treating agent, water-dispersible silica, and one or more of a zirconium or titanium compound, thiocarbonyl compound, and a water-soluble acrylic resin. The metallic surface treating agent is selected from a provided list of silane coupling agents that are typically used in the coating industry to improve adhesion between the pre-coating and the decorative coating.

[0008] U.S. Patent No. 5,859,106 to Jones et al. describes a non-chrome coating composition that contains a cross-linked polymer system, which includes a copolymer with acrylic and hydroxyl functionality or the reaction product of an acrylic polymer and a polymer with hydroxyl functionality. A fluoroacid such as fluorozirconic acid or fluorotitanic acid can be added to these compositions. U.S. Patent No. 5,905,105 to Jones et al. describes a non-chrome coating composition that includes the coating composition described in U.S. 5,859,106 with the addition of dispersed silica and an ammonium carbonate containing a group IVB metal.

[0009] Some of the above compositions can also be used to prepare metal surfaces for cold working. For example, one conventional method is to apply a heavy zinc phosphate coating to the surface and then apply a composition containing an alkali metal soap, usually sodium stearate, which reacts with the zinc content of the zinc phosphate coating to form a very effective lubricant layer that is believed to contain zinc soap. This practice produces excellent results, but current environmental concerns militate against the use of zinc and other heavy metals such as nickel, manganese, and calcium, which are often required to obtain the best lubricant properties when using this technique. The metal soap containing coatings formed on metal surfaces in this way are also sources of a substantial dust nuisance in many cases.

[0010] Decades ago, iron phosphating was commonly used as a basis for lubricant layers for cold working metals, but the thicker layers provided by zinc phosphating generally have been found to produce more effective lubrication and thus

are highly preferred. Conventional aqueous iron phosphating treatment compositions contain primarily alkali metal or ammonium phosphates, sometimes additional phosphoric acid, and usually some kind of accelerator as their active ingredients. There remains an interest to develop improved coating compositions to provide a lubricating coating on a metal substrate prior to cold-working the substrate.

Summary of the Invention

[0011] The invention is directed to a process of forming on a metal substrate a composition prior to the substrate being cold worked. The process includes a step of contacting the substrate with an aqueous composition comprising acid-stable particles and one or more fluoroacids. The amount of the acid-stable particles in the coating composition is from 0.005% to 8% by weight on a dry weight basis.

Brief Description of the Drawings

[0012] The invention will be better understood by reference to the Detailed Description of the Invention when taken together with the attached drawing, wherein

[0013] Figure 1 is a plot of coating weights and compositions on CRS panels vs. spray time for coatings provided by a coating composition of the invention;

[0014] Figure 2 is a plot of coating weights on CRS panels vs. spray time for coatings provided by other coating compositions of the invention; and

[0015] Figure 3 is yet another a plot of coating weights on CRS panels vs. spray time for coatings provided by still other coating compositions of the invention.

Detailed Description of the Invention

[0016] The invention is directed to a process of forming on a metal substrate a composition prior to the substrate being cold worked. The process comprises a step of contacting the substrate with an aqueous composition comprising acid-stable particles and one or more fluoroacids, wherein the amount of the acid-stable particles in the coating composition is from 0.005% to 8% by weight on a dry weight basis. The process provides protection to metal substrates, e.g., ferriferous substrates, as the substrates are cold-worked. In particular, the process is particularly advantageous in the drawing of metal substrates to form wires, piping or thin-walled tubing.

[0017] The process can also include pre-treating the substrate with an alkaline cleaner and an acidic pickle solution. The term "pre-treating" refers to the treatment

of the substrate prior to contacting the substrate with the coating composition comprising the acid-stable particles. A treated substrate is a substrate that has been contacted with the coating composition comprising the acid-stable particles.

[0018] The process can also include post-treating of the treated substrate. The term "post-treating" refers to the contacting of the treated substrate with another composition. In particular, a treated substrate can be contacted with a naphthenic oil emulsion at a temperature of at least 120 °C. This oil treatment is typically followed by heating the substrate at a temperature of at least 200 °C.

[0019] The coating composition comprises an aqueous mixture comprising acid-stable particles and one or more fluoroacids. The aqueous mixture can also contain a product of the acid-stable particles and the one or more fluoroacids. Particles are acid-stable if the change in viscosity as measured in a test sample, as described herein under the subheading, "Test procedure for acid-stable particles", is ten seconds or less, preferably five seconds or less. In most cases, test samples that correspond to the acid stable particles of the invention will have a change in viscosity of three seconds or less. In the most preferred embodiments, the acid-stable particles will have a change in viscosity of one second or less. Typically, the lower the change in viscosity the more stable the particles are in acid, that is, in an aqueous solution with a pH of 3 to 7.

[0020] The term "change in viscosity" used herein reflects the viscosity measurement made in accordance to the described test procedure. With respect to some of the compositions of the invention, their corresponding test samples can over 96 hours actually decrease in viscosity such that the measured change in viscosity is less than zero.

[0021] Alternatively, one of ordinary skill can determine if particles are acid-stable by preparing an acidified test sample containing the particles as described, and simply observing whether there is any visible indication of thickening, precipitation or gelling over about 96 hours at room temperature.

[0022] Typically, the acid-stable particles of the invention will maintain a negative charge at a pH from about 2 to about 7. In some cases, the acid-stable particles will maintain a negative charge at a pH from about 3 to about 6. In still other cases, the acid-stable particles will maintain a negative charge at a pH from about 3.5 to about 5.

[0023] One way to determine whether the acid-stable particles retain a negative charge is by measuring the Zeta Potential of the particles. This measurement can be carried out using commercially available instruments such as a Zetasizer 3000HSA from Malvern Instruments Ltd. A negative measured voltage indicates the particles are negatively charged. Exemplary Zeta Potentials for silica-based, acid-stable particles used in the coating compositions are -5 to -35 mV. Exemplary Zeta Potentials for the organic, polymeric acid-stable particles used in the coating compositions are -55 to -85 mV.

[0024] The coating composition of the invention also contains water. Water is used to dilute the coating composition of the invention, and provides relatively long-term stability to the composition. For example, a composition that contains less than about 40% by weight water is more likely to polymerize or "gel" compared to a coating composition with about 60% or greater by weight water under identical storage conditions. Although the coating compositions of the invention typically applied to the substrate will contain about 92% water or greater, it is to be understood that a coating composition of the invention also includes a concentrated formulation composition with 60% to 92% by weight water. The end-user simply dilutes the concentrated formulation with additional water to obtain an optimal coating composition concentration for a particular coating application.

[0025] The coating composition of the invention can be provided as a ready-to-use coating composition, as a concentrated coating composition that is diluted with water prior to use, as a replenishing composition, or as a two component coating system. In a two-component coating system the fluoroacid is stored separately from the particles. The fluoroacid and the particles are then mixed prior to use by the end-user.

[0026] The concentration of each of the respective components of the coating compositions will, of course, be dependent upon whether the coating composition to be used is a replenishing coating composition, a concentrated coating composition, or a ready-to-use coating composition. A replenishing coating composition can be provided to and used by an end-user to restore an optimal concentration of components of a coating composition to a coating bath as the components are consumed during the coating of substrates. As a result, a replenishing coating

composition will necessarily have a higher concentration of acid-stable particles or fluoroacids than the coating composition used to coat the substrate.

[0027] The concentration of acid-stable particles in the compositions of the invention depends on the type of particles used and the relative size, e.g., average diameter, of the particles. The coating compositions will contain from 0.005% to 8% by weight, 0.006% to 2% by weight, 0.007% to 0.5% by weight, or from 0.01% to 0.2% by weight, on a dry weight basis of acid-stable particles.

[0028] Acid-stable silica particles can be aluminum-modified silica particles. Aluminum-modified silica particles will have a weight ratio of $\text{SiO}_2:\text{Al}_2\text{O}_3$ from about 80:1 to about 240:1, and from about 120:1 to about 220:1. The concentration of aluminum-modified silica particles in the compositions of the invention is from 0.005% to 5% by weight, 0.006% to 1% by weight, 0.007% to 0.5% by weight, or from 0.01% to 0.2% by weight, on a dry weight basis of acid-stable particles.

[0029] In one embodiment, the acid-stable particles used in a coating composition are silica particles provided as a colloidal suspension from Grace Davison under the trademark Ludox[®] TMA, Ludox[®] AM, Ludox[®] SK, and Ludox[®] SK-G. These specific types of silica particles are treated with an aluminum compound, believed to be sodium aluminate. For example, Ludox[®] AM has a weight ratio of $\text{SiO}_2:\text{Al}_2\text{O}_3$ from about 140:1 to 180:1. Aluminum-modified silica such as Adelite[®] AT-20A obtained from Asahi Denka can also be used.

[0030] The acid-stable particles can be relatively spherical in shape with an average diameter from about 2 nm to about 80 nm, or from about 2 nm to about 40 nm, as measured by transmission electron microscopy (TEM). The particles can also be rod-shaped with an average length from about 40 nm to about 300 nm, and an average diameter from about 5 nm to about 20 nm. The particles can be provided as a colloidal dispersion, e.g., as a mono-dispersion in which the particles have a relatively narrow particle size distribution. Alternatively, the colloidal dispersion can be poly-dispersed in which the particles have a relatively broad particle size distribution.

[0031] The silica particles are typically in the form of discrete spheres suspended in an aqueous medium. The medium can also contain a polymer to improve stability of the colloidal suspension. The polymer can be one of the listed polymers provided below. For example, certain commercially available formulations

include a polymer to maintain stability of the dispersion during storage. For example, Ludox[®] SK and Ludox[®] SK-G are two commercial forms of colloidal silica that contain a polyvinyl alcohol polymer.

[0032] It is to be understood, that the coating compositions do not require the presence of a polymer to maintain acid stability of the compositions at a pH from 2 to 7. However, in some applications, a polymer can be added to the coating compositions to provide even greater acid stability.

[0033] As indicated by the comparative coating compositions the use of Ludox[®] AS, Ludox[®] HS, and Ludox[®] TM silica particles do not provide acid-stable coating compositions, and thus are not acid-stable particles. That is not to say that these non acid-stable particles cannot be present in the coating compositions of the invention in relatively small amounts. It is to be understood, that the amount or concentration of non acid-stable particles that can be present in the coating compositions will depend upon the type of non acid-stable particles, the pH of the composition, the type of fluoroacid used, and the type and concentration of acid-stable particles in the composition. Of course, one of ordinary skill would also recognize that one or more different types of acid-stable silica particles can be combined in a coating composition of the invention.

[0034] In another embodiment, the acid-stable particles can be nonaluminum-modified silica particles. These silica particles are modified by some process, at times a proprietary process, that is not considered by those skilled in the art to be an aluminum modification process. The nonaluminum-modified silica particles are negatively charged and have a majority of silicon acid sites neutralized, for example, by sodium or ammonia. Examples of nonaluminum-modified silica particles that can be used in the coating compositions include colloidal particles from Nissan Chemical sold under the trademark Snowtex[®] O and Snowtex[®] N. The concentration of nonaluminum-modified silica particles in the compositions of the invention is from 0.005% to 5% by weight, 0.006% to 1% by weight, 0.007% to 0.5% by weight, or from 0.01% to 0.2% by weight, on a dry weight basis of acid-stable particles.

[0035] In another embodiment, a selection of organic, polymeric acid-stable particles can be used in the coating compositions. For example, polymeric particles selected from the group consisting of anionically stabilized polymer dispersions, such

as epoxy-crosslinked particles, epoxy-acrylic hybrid particles, acrylic polymer particles, polyvinylidene chloride particles, and vinyl acrylic/vinylidene chloride/acrylic particles provide acid-stable coating compositions. Three commercially available polymeric particles that can be used include ACC 800 and ACC 901 from Henkel Corp., and Haloflex[®] 202 from AVECIA, Inc. ACC 901 includes epoxy-crosslinked particles. ACC 800 includes polyvinylidene chloride particles. Haloflex[®] 202 includes vinyl acrylic/vinylidene chloride/acrylic particles. The concentration of organic polymeric particles in the compositions of the invention is from 0.01% to 8% by weight, from 0.01% to 5% by weight, and from 0.1% to 3% by weight, on a dry weight basis.

[0036] The fluoroacid is an acid fluoride or acid oxyfluoride with an element selected from the group consisting of Ti, Zr, Hf, Si, Sn, Al, Ge and B. The fluoroacid should be water-soluble or water-dispersible and preferably comprise at least 1 fluorine atom and at least one atom of an element selected from the group consisting of Ti, Zr, Hf, Si, Sn, Al, Ge or B. The fluoroacids are sometimes referred to by workers in the field as "fluorometallates".

[0037] The fluoroacids can be defined by the following general empirical formula (I):



wherein: each of q and r represents an integer from 1 to 10; each of p and s represents an integer from 0 to 10; T represents an element selected from the group consisting of Ti, Zr, Hf, Si, Sn, Al, Ge, and B. Preferred fluoroacids of empirical formula (I) include: T is selected from Ti, Zr, or Si; p is 1 or 2; q is 1; r is 2, 3, 4, 5, or 6; and s is 0, 1, or 2.

[0038] One or more of the H atoms may be replaced by suitable cations such as ammonium, metal, alkaline earth metal or alkali metal cations (e.g., the fluoroacid can be in the form of a salt, provided such salt is water-soluble or water-dispersible). Examples of suitable fluoroacid salts include $(NH_4)_2SiF_6$, $MgSiF_6$, Na_2SiF_6 and Li_2SiF_6 .

[0039] The preferred fluoroacids used in the coating compositions of the invention are selected from the group consisting of fluorotitanic acid (H_2TiF_6), fluorozirconic acid (H_2ZrF_6), fluorosilicic acid (H_2SiF_6), fluoroboric acid (HBF_4), fluorostannic acid (H_2SnF_6), fluorogermanic acid (H_2GeF_6), fluorohafnic acid

(H_2HfF_6), fluoroaluminic acid (H_3AlF_6), and salts of each thereof. The more preferred fluoroacids are fluorotitanic acid, fluorozirconic acid, fluorosilicic acid, and salts of each thereof. Some of the salts that can be used include alkali metal and ammonium salts; e.g., Na_2MF_6 and $(\text{NH}_4)_2\text{MF}_6$, where M is Ti, Zr, and Si.

[0040] The concentration of the one or more fluoroacids in the coating compositions of the invention can be relatively quite low. For example, a fluoroacid concentration of about 5 ppm can be used, and still provide corrosion resistant coatings (ppm = parts per million). The concentration of the one or more fluoroacids in the coating compositions is from about 5 ppm (about 0.0005% by weight) to about 10,000 ppm (about 1.0% by weight), from about 5 ppm to about 1000 ppm and from 5 ppm to about 400 ppm. The preferred concentrations of the one or more fluoroacids in the coating compositions is from about 3 ppm to about 3000 ppm, more preferably from about 10 ppm to about 400 ppm. The final concentration, of course, will depend upon the amount of water used to prepare the coating compositions of the invention.

[0041] The addition of catechol compounds in the coating compositions can be used to provide a visible color indicator that the metal substrate is indeed coated. Without the catechol compound, the resulting coatings can be, at times, too thin to be visible. The term "catechol compound" is defined as an organic compound with an aromatic ring system that includes at least two hydroxyl groups positioned on adjacent carbon atoms of the aromatic ring system.

[0042] The preferred catechol compounds used to prepare the coating compositions of the invention are negatively charged or neutral, that is, have no charge. The negatively charged catechol compounds are commonly available as metal salts, particularly as alkali or alkaline earth metal salts.

[0043] The concentration of catechol compound in the coating compositions of the invention can be optimized by those skilled in the art to provide a visible coating. The concentration of the catechol compound will depend on the type of catechol compound used. Also, each catechol compound can be expected to have a different interaction with each type of acid-stable particles used in the coating composition. As a result, the optimal concentration of catechol compound depends upon which type(s) of acid-stable particles are used in the coating compositions. Lastly, because any excess catechol compound can be removed with a rinse step

following application of the coating composition to a metal substrate, the concentration of the catechol compound can be greater than what is required to provide a visibly colored coating.

[0044] In one embodiment, the catechol compound is selected from the alizarin series of compounds. For example, alizarin, alizarin red, alizarin orange, and the salts of each thereof can be used to prepare the coating compositions of the invention. One preferred alizarin compound is alizarin red, i.e., 3,4-dihydroxy-9,10-dioxo-2-anthracenesulfonic acid or the salt thereof.

[0045] In another embodiment, the catechol compound is selected from pyrocatechol, and conjugated pyrocatechols. The term "conjugated pyrocatechol" is defined as pyrocatechol with a conjugated ring system. Pyrocatechol sulfonephthalein, i.e., pyrocatechol violet, or the salts thereof, is one preferred conjugated pyrocatechol.

[0046] The coating compositions of the invention can also include one or more polymers. The one or more polymers preferably comprise functional groups selected from hydroxyl, carboxyl, ester, amide, or combinations thereof. The functional groups on the polymers are believed to serve various functions. First, prior to forming the coatings, the functional groups provide a polymer that has a relatively high solubility or miscibility in water. Second, the functional groups provide points along the polymer backbone through which cross-linking between the polymers can occur as the coating composition cures to form a coating on a metal substrate. Third, the functional groups on the polymer are believed to enhance binding between the metal substrate and particles in the cured coating.

[0047] An exemplary list of the one or more polymers used are selected from polyvinyl alcohol, polyester, water-soluble polyester derivatives, polyvinylpyrrolidone, polyvinylpyrrolidone-vinylcaprolactam copolymer, polyvinylpyrrolidone-vinylimidazole copolymer, and sulfonated polystyrene-maleic anhydride copolymer. The most preferred polymers used include polyvinyl alcohol, polyvinylpyrrolidone-vinylcaprolactam copolymer. Luvitec[®] and Elvanol[®] are two commercially available types of polymers that can be used to prepare a coating composition of the invention. Luvitec[®] is a vinylpyrrolidone-vinylcaprolactam polymer available from BASF. Elvanol[®] is a polyvinyl alcohol polymer available from Dupont.

[0048] In the presence of one or more of the above polymers, the fluoroacids can function as a curing agent as well as a binding agent. It is believed that the fluoroacid reacts with the functional groups of the polymer, and thus can provide a means for the polymer to cross-link. The cross-linking of the polymer in combination with the fluoroacid provides a cement-like polymer-metal oxide matrix that binds the particles to form a coating on a metal substrate.

[0049] A coating composition of the invention is prepared by a process comprising: providing acid-stable particles and one or more fluoroacids; and mixing the acid-stable particles and the one or more fluoroacids in water. The amount of acid-stable particles in the coating composition is from 0.005 to 8% by weight on a dry weight basis. Preparation of the coating composition can also include one or more polymers exemplified in the list above, and mixing the polymer with the other components.

[0050] The pH of a coating composition of the invention ranges from about 2 to about 7, preferably from about 3 to about 6, and more preferably from about 3.5 to about 5. The pH of the coating composition can be adjusted using mineral acids such as hydrofluoric acid, phosphoric acid, and the like, including mixtures thereof. Alternatively, additional amounts of the fluoroacids can be used. Organic acids such as lactic acid, acetic acid, citric acid, sulfamic acid, or mixtures thereof can also be used.

[0051] If the composition is to be applied to a substrate that is to be cold-worked, the composition will typically have a pH from 4.5 to 5.5. For ferriferous metal substrates the composition will typically have a pH from 4.7 to 5.3.

[0052] The pH of the coating composition can also be adjusted by adding small amounts of an alkali material, typically in the form of a metal or ammonium hydroxide, carbonate, or bicarbonate. Exemplary inorganic and organic bases include sodium hydroxide, ammonium hydroxide, ammonia, or amines, e.g., triethanolamine or other alkylamines.

[0053] The coating compositions can also include one or more secondary agents selected from a leveling agent, a wetting agent, an antifoaming agent, and a bonding agent. However, one of ordinary skill would understand that the use of such agents, and the concentrations at which they are used, must be compatible within the

pH range of the coating composition. The addition of too much of a secondary agent could significantly diminish the acid stability of the compositions.

[0054] The coating composition of the invention can be applied to a metal substrate to form a corrosion resistant coating. Metal substrates that can be passivated (provided with enhanced corrosion resistance) by the coating compositions of the invention include cold rolled steel, hot-rolled steel, stainless steel, steel coated with zinc metal, zinc alloys such as electrogalvanized steel, galvalume, galvaneal, and hot-dipped galvanized steel, aluminum alloys and aluminum plated steel substrates. The invention also offers the advantage that components containing more than one type of metal substrate can be passivated in a single process because of the broad range of metal substrates that can be passivated by the coating compositions of the invention.

[0055] Although not necessary, the metal substrate is usually cleaned to remove grease, dirt, or other extraneous materials by using conventional cleaning procedures and materials, e.g., mild or strong alkaline cleaners. Examples of alkaline cleaners include Parco[®] Cleaner ZX-1 and Parco[®] Cleaner 315, both of which are available from Henkel Surface Technologies. The metal substrate is then rinsed with water or an aqueous acidic solution. The metal substrate can also be treated with a commercially available metal phosphate solution, e.g., iron or zinc phosphate solutions, prior to contacting the metal substrate with a coating composition of the invention.

[0056] A coating composition of the invention is applied to the metal substrates in any number of ways known in the art. Two of the most preferred methods are spraying and immersion. The thickness and composition of the cured coating on the metal substrate depends on a number of factors including particle size, particle concentration, and exposure time or time in contact with the coating composition.

[0057] Figure 1 is provided to show how the composition of a dried coating on a CRS panel prepared from the coating composition of Example 1 can change with spray time. As shown, the concentration of silica (weight of silicon and oxygen) in the coating is relatively independent of spray time, that is, the amount of silica is relatively constant at about 14 to 17 mg/sq ft over a spray time of about 25 to 100

seconds. This would be expected given the proposed monolayer structure of the coating.

[0058] Figures 2 and 3 depict differences in the thickness coatings over a spray time of about 25 to 125 seconds for selected coating compositions of the invention.

[0059] In contrast, the amount of titanium and zirconium in the coating is shown to increase linearly with time. The amount of metal in the coating is from 0.5 mg/sq ft to 6 mg/sq ft. In many instances, the amount of metal in the coatings is from 0.5 mg/sq ft to 3 mg/sq ft.

[0060] The coatings resulting from the compositions of the invention are relatively low weight coatings when compared to present coating technologies. The coatings of the invention have a coating weight from 5 mg/sq ft to 50 mg/sq ft. In many instances, however, the coatings will have a coating weight from 8 mg/sq ft to 30 mg/sq ft. In fact, coatings with a coating weight from 8 mg/sq ft to 20 mg/sq ft are typically formed from the coating compositions. The amount of coating on the substrate is determined by conventional stripping of the formed coating in a solution of 0.5% CrO₃ in water.

[0061] If the coating composition is applied to a metal substrate that is to be cold worked, the amount of time the substrate remains in contact with the aqueous composition substrate, e.g., in an immersion bath, depends upon the metal substrate and the degree of cold-working to be performed. Typically, the substrate remains in an immersion bath for a time sufficient to form at least about 0.1 g/m² of a water insoluble conversion coating on the substrate. Some applications require thicker coatings and therefore longer contact times or selected bath conditions. In some cases, the substrate remains in an immersion bath for a time sufficient to form at least about 0.3 g/m² of a water insoluble conversion coating on the substrate.

[0062] In other applications still thicker coatings are required and contacting of the substrate with the aqueous composition is conducted for a time sufficient to form at least about 0.6 g/m², and in some cases for a time sufficient to form at least about 1.0 g/m², of a water insoluble conversion coating on the substrate.

[0063] Following treatment of a metal substrate with a coating composition, the coating composition can be dried in place on the surface of the metal substrate.

Alternatively, the applied coating composition can be rinsed, preferably with water, to remove excess coating composition, and then dried. The drying can be done at any temperature. Typical convenient temperatures are from 100 °F to 300 °F. The drying conditions selected depend upon the customer's preferences, space available, and the type of finish coating used. For example, a powder coating typically requires a dry surface prior to application compared to a water-based coating.

[0064] If the metal substrate is to be cold-worked, irrespective of whether or not a coating formed by the process according has been rinsed before being dried, the dried coating may be, and usually preferably is, coated with additional lubricant materials known per se in the art before being cold worked. A wide variety of oils and greases, along with other materials, are known for this purpose. A particularly preferred supplemental lubricant of this type includes as a principal constituent ethoxylated straight chain aliphatic alcohol molecules, wherein the initial alcohol molecules have a single --OH moiety and at least 18 carbon atoms. The molecules of this supplemental lubricant preferably have a chemical structure that can be produced by condensing ethylene oxide with primary, most preferably straight chain, aliphatic monoalcohols that have, with increasing preference in the order given, at least 25, 30, 35, 40, 43, 46 or 48 carbon atoms per molecule and independently, with increasing preference in the order given, not more than 65, 60, 57, 55, 52, or 51 carbon atoms per molecule. Independently, these actual or hypothetical precursor aliphatic alcohols preferably have no functional groups other than the single --OH moiety, and, optionally but less preferably, also fluoro and/or chloro moieties. Independently, it is preferred that these molecules of ethoxylated alcohols contain, with increasing preference in the order given, at least 20, 30, 35, 40, 43, 47, or 49%, and independently preferably contain, with increasing preference in the order given, not more than 80, 70, 62, 57, 54, or 51%, of their total mass in the oxyethylene units. This preferred type of supplemental lubricant can readily be obtained in the form of dispersions in water for convenient application over a dried coating formed by a primary process according to this invention. Preferred compositions and methods for using them are described in U.S. Pat. Nos. 5,368,757 of Nov. 29, 1994 to King, 5,531,912 of Jul. 2, 1996 to Church et al., and 5,547,595 of Aug. 20, 1996 to Hacias and in PCT Application US95/05010 filed Apr. 26, 1995 and published as WO 95/31297.

[0065] The coating comprises acid-stable particles attached to the metal substrate through a metal-oxide matrix. In the context of a cured coating on a metal substrate, the use of the term "acid-stable" particle to describe the particle in the coating refers to particles that provide acid-stable coating compositions defined herein. The metal-oxide matrix comprises one or more metals selected from the group consisting of titanium, zirconium, silicon, hafnium, boron, aluminum, germanium, and tin. The metal-oxide matrix preferably comprises one or more metals selected from titanium, zirconium, and silicon. If a water soluble polymer is present in the coating composition, the metal-oxide matrix can further contain a reaction product of the one or more polymers and the one or more fluoroacids or salts of each thereof. The coating of the invention can be described as a brick and mortar coating with the particles represented by the bricks and the metal oxide matrix represented by the mortar.

[0066] One advantage of the coatings of the invention is that they provide comparable and, in most instances, improved corrosion resistance relative to present iron phosphate coating technology. Also, this improvement in corrosion resistance is achieved with a coating coverage that is significantly less than present iron phosphate coatings. For example, to provide an acceptable degree of corrosion resistance to a CRS panel, iron phosphate coatings are applied at a coverage level from about 50 mg/sq ft to 150 mg/sq ft. In contrast, a coating of the invention can provide a similar degree of corrosion resistance at a coverage level from 8 mg/sq ft to 30 mg/sq ft. In most cases, a coating of the invention exhibits an acceptable degree of corrosion resistance at coverage levels from 8 mg/sq ft to 20 mg/sq ft.

[0067] Another advantage of the coatings of the invention over iron phosphate coatings is exhibited through its relatively high flexibility and durability. In impact tests and bending tests the coatings of the invention typically maintain their corrosion resistance while the iron phosphate coatings do not. Moreover, these tests were performed with coatings of the invention at coverage levels of less than 20 mg/sq ft, while the iron phosphate coatings had coverage levels of about 65 mg/sq ft.

[0068] Additional coatings can then be applied. In most cases, these coatings can be a primer paint composition or a final paint coating such as a finish coat. One of the many advantages of the coatings of the invention is that the coatings are

compatible with any number of protective paints such as Duracron[®] 200, which is a high solid, acrylic paint from PPG Industries, and powder paints such as Sunburst[®] Yellow, which is a polyester powder paint from Morton International. The coatings of the invention are also compatible with paints that are applied by electrodeposition.

[0069] The invention and its benefits will be better understood with reference to the following examples. These examples are intended to illustrate specific embodiments within the overall scope of the invention as claimed, and are not to be understood as limiting the invention in any way.

1. Test procedure for acid-stable particles.

[0070] Prepare a sodium acetate/acetic acid buffer with a pH of about 5.0 by acidifying the solution with hydrochloric acid. To 20 mL of buffer solution add 20 mL of the selected particle dispersion. As a test sample, the particle dispersion should have a silica concentration of about 30 wt%. If the selected particle dispersion has a higher wt%, dilute the dispersion to 30 wt%. Stir the solution for ten minutes. Observe whether the solution remains fluid, that is, whether there is any visible indication of thickening, precipitation or gelling over about 96 hours at room temperature.

[0071] An experimental method used to qualitatively define acid-stable particles is to measure the change in viscosity of a test sample above after 84 hours at room temperature. Applicants measure the change in viscosity using a Zahn Cup apparatus from Gardner Laboratory Division, Pacific Scientific Co.

[0072] The Zahn viscosity cup is a small U-shaped cup suspended from a wire. The cup has an orifice, which is available in various sizes, at its base. For example, the #2 Zahn cup used in the acid stability test is certified to ASTM D4212 with an orifice diameter of 2.69 mm. The viscosity of a sample is measured by completely submerging the cup into the test sample. The cup is then completely withdrawn from the sample. The time in seconds from the moment the top of the cup emerges from the sample until a portion of the stream breaks free from the stream falling through the orifice is the measure of the viscosity of the sample.

[0073] Following the acid-stability procedure described above, a sodium acetate/acetic acid buffer with a pH of about 5.0 was prepared. 20 mL of the selected particle dispersion was added to 20 mL of the buffer solution. The particle dispersion should have a silica concentration of about 30 wt%. If the selected particle dispersion

has a higher wt%, dilute the dispersion to 30 wt%. Stir the solution for ten minutes. The fresh viscosity measurement was made at about this time.

[0074] Each sample is then allowed to sit at about room temperature until the next viscosity measurement is made. As shown in Table 1, there was little, if any, change in viscosity for test samples prepared from the particles of Examples 1-10 at 96 hours. In comparison, Comparative Examples 1-4 are observed to thicken or gel over 96 hours. Because these samples had gelled at 96 hours, the final viscosity measurement was made after 84 hours, Table 2.

2. Preparation of the metal substrates.

[0075] Panels of cold-rolled steel and electrogalvanized steel used to test the corrosion resistance of the cured coatings are pretreated as follows. The panels are treated with Parco Cleaner 1523, which is an alkaline cleaner available from Henkel Surface Technologies. The panels are sprayed with the cleaner (about 2% in water) at 120 °F for 2 minutes. The cleaned panels are rinsed with a warm tap water spray for 30 seconds. A coating composition of the invention is sprayed on the rinsed panels for 30 seconds at ambient temperature. Alternatively, the panels are immersed in the coating compositions. The coated panels are then optionally rinsed with a cold water spray rinse for 30 seconds. Typically, if a relatively high particle content coating composition of the invention is used, a water rinse will follow to remove residual (unbound) particles from the panels. The water rinse is not usually necessary for relatively low particle content coating compositions. The panels are then dried at 300 °F for 5 minutes. Coating weight of this invention was obtained by measuring the metal content, e.g., silicon, titanium, and zirconium, using x-ray fluorescence of the coated panels. Silica coating weight can also be measured by the weigh-coat-weigh-strip-weigh procedure, where the invention is stripped by 45% potassium hydroxide at 170 °F.

Table 1

Ex.	Acid stable particle	viscosity (fresh) sec.	viscosity (96 hrs) sec.	Δ , change in viscosity
1	Ludox TMA	14	15	1
2	Ludox AM	14	14	0
3	Ludox SK	14	14	0
4	Ludox SK-G	14	14	0
5	Snowtex C	14	15	1
6	Snowtex O	14	14	0
7	Snowtex N	14	15	1
8	ACC 800	14	14	0
9	Haloflex 202	15	15	0
10	ACC 901	15	15	0

Table 2

Comp. Ex.	Non-acid stable particle	viscosity (fresh) sec.	viscosity (84 hrs) sec.	Δ , change in viscosity	after 96 hr
1	Cabospere A-205	14	30	16	gel
2	Luodx AS-30	15	96	81	gel
3	Snowtex 40	14	112	98	gel
4	Snowtex OUP	14	65	51	gel

3. Application of finish coat on coated substrates.

[0076] The coated and dried panels are painted with Duracron 200, a polyacrylic enamel coating commercially available from PPG Industries, Inc., or Sunburst Yellow, an epoxy-polyester hybrid powder paint commercially available from Morton International. The painted panels are allowed to cure according to recommendations by the manufacturer.

4. Corrosion tests.

[0077] To test the corrosion resistance of the panels, the panels are scribed and a salt solution (5% NaCl) is sprayed on the scribed panels for either 500 hr or 750 hr (ASTM B-117 method). The corrosion resistance of the coated panels is evaluated by measuring the creepage from the scribe. The data reported in Table 3 is the distance in mm of the widened scribe following corrosion by the spray solution on CRS panels. As a result, the smaller the number, the more effective the corrosion resistance of the coating.

Example 1.

[0078] Fluorotitanic acid (0.4 g, 60%) and fluoro-zirconic acid (0.4 g, 20%) are added to stirred distilled water (3989.2 g). As this mixture is stirred, 10 g of Ludox[®] TMA (33% silica) is added. The pH of this mixture is adjusted to about 4 by adding ammonium carbonate and/or small amounts of additional fluorotitanic acid. The mixture is stirred for about two hours.

Examples 2 to 10.

[0079] Examples 2 to 10 are coating compositions prepared according to the procedure of Example 1 with the exception of the type and the concentration of acid-stable particle used. The type and weight percent of particles for Examples 1 to 10 is provided in Table 4. The weight percent of fluorotitanic acid and fluoro-zirconic acid in Examples 2 to 10 is about 0.01%.

Table 3.

Coating	Scribe creep (mm) ^a	Scribe creep (mm) ^b	Coating weight mg/sq ft
Bonderite 1090 with PLN 99A seal	4.2	4.2	60
Example 1	3.6	4.2	15
Example 10	2.2	2.9	16

^a 500 hour salt spray, paint is Duracron 200.

^b 750 hour salt spray, paint is Sunburst Yellow.

Bonderite B-1090 and PLN 99A are iron phosphite and polymer rinse from Henkel Corp.

Table 4.

Ex.	Particle type and wt%	Pass Acid Stability Test	Coating thickness ^a (nm)	Particle size ^b (nm)	Surface modified	Coating weight mg/sq ft
1	0.25% Ludox [®] TMA	Yes	73	60	aluminum	15
2	0.25% Ludox [®] AM	Yes	44	35	aluminum	9
3	0.25% Ludox [®] SK	Yes	44	35	aluminum	9
4	0.25% Ludox [®] SK-G	Yes	97	30	aluminum	20
5	1% Snowtex [®] C	Yes	44	31	aluminum	9
6	1% Snowtex [®] O	Yes	55	33	Proprietary	10.5
7	1 % Snowtex [®] N	Yes	97	35	Proprietary	20
8	0.5% ACC 800	Yes	103	95	n/a	11.5
9	0.5% Haloflex 202	Yes	155	201	n/a	17.3
10	2% ACC 901	Yes	143	177	n/a	16

^a A density of 2.2 for silica particle and 1.2 for organic polymeric particles was used with the measured coating weight to obtain film thickness values. Silica particles are stripped with 45% KOH at 170 °F. Polymeric particles were dried at 120 °F and then acetone stripped. For Example #1, the coating thickness was estimated from the following calculation with silica coating weight of 15 mg/sqft and density of 2.2 g/cubic centimeter:

$$15 \frac{mg}{sqft} \cdot \frac{g}{1000mg} \cdot \frac{sqft}{0.093sqmeter} \cdot \frac{sqmeter}{10000sqcentimeter} \cdot \frac{g}{2.2cubic.centimeter} \approx 73 \times 10^{-7} \text{ centimeter} = 73nm$$

Examples 11 to 16

[0080] Examples 11 to 16 are coating compositions prepared according to the procedure of Example 1 with the exception of the concentration of acid-stable particle, titanium and zirconium used. The weight percents of particles, titanium, and zirconium for Examples 11 to 16 are provided in Table 5. The titanium and zirconium were provided in the form of fluorotitanic and fluorozirconic acid. The titanium, zirconium and silica contents were measured by inductively coupled plasma (ICP) spectroscopy.

Examples 17 to 20

[0081] Examples 17 to 20 are coating compositions prepared according to the procedure of Example 1 with the exception of the concentration of acid-stable particle

used, and the concentration of zirconium. The weight percents of particles and zirconium for Examples 17 to 20 are provided in Table 6.

Table 5

Example	silica %	Ti %	Zr %	Scribe creep (mm)			Coating weight mg/sq ft
				CRS/ Duracron 200, 500 hr NSS	EG /Duracron 200, 20 cycles GM9540P	CRS /Sunburst Yellow, 750 hrs NSS	
B-1090/PLN99A	N/A	N/A	N/A	4.5	1.8	6	60
11	0.435	0.0144	0.0093	3.8	0.4	5.2	29.8
12	0.434	0.0098	0.0093	3.6	0.6	5.0	32
13	0.426	0.0088	0.009	4	0.8	5.8	26.6
14	0.439	0.0084	0.0088	3.9	0.6	5.6	20.6
15	0.425	0.0084	0.0088	4.4	0	5.0	17.1
16	0.409	0.0073	0.0084	4.2	0.2	5.8	16.7

Comparative Examples 1 to 6.

[0082] Comparative Examples 1 to 3 are coating compositions containing Ludox[®]-type silica particles. Comparative Examples 4 and 5 are coating compositions containing Snowtex[®]-type silica particles. Comparative Example 6 is a coating composition containing Cabosphere[®] A-205 silica particles.

[0083] Comparative Examples 1 to 6 are prepared according to the procedure of Example 1 with the exception of the type of silica particles used. The weight percent of fluorotitanic acid and fluorozirconic acid is about 0.01%. Comparative Examples 1 to 6 do not contain acid-stable particles, and attempts to use these compositions failed to provide any coating to the panels. Comparative Examples 1 to 6 are summarized with the corresponding coating data in Table 7.

Table 6

Example	Silica %	Zr %	Scribe creep (mm)				Coating weight, mg/sq ft
			CRS/ Duracron 200, 500 hr NSS	CRS /Duracron 200, 20 cycles GM9540P	CRS /Sunburst Yellow, 750 hrs NSS	CRS/ Sunburst Yellow, 40 cycles GP9540P	
B-1090/ PLN99A	N/A	N/A	3.9	3.2	7.6	7	57
17	0.0059	0.004	4.2	2.8	7.1	7.1	28.4
18	0.013	0.008	3.2	2.6	6.9	6.9	24.3
19	0.013	0.009	3.4	2.7	7.3	7.3	33.3
20	0.016	0.011	3.2	2.7	6.7	6.7	27.1

Table 7

Comparative Ex. No.	Particle type and wt%	Pass acid stability test	Surface modified	Particle size (nm)
1	0.25% Ludox [®] AS-30	No	no	12
2	0.25% Ludox [®] HS	No	no	12
3	0.25% Ludox [®] TM	No	no	20
4	Snowtex 40	No	no	15
5	Snowtex 50	No	no	25
6	Cabosperser A-205	No	no	150

Cold-Working of Metal Substrates: Drawing Operation

[0084] The coating line coats bundles of 80-100 tubes per lift. Tow sizes of mother tubes are drawn; both are annealed, 1010C steel from Metal Matic, the smaller is 1 1/2" OD and the larger 2" OD. The tubes are drawn 3-at-a-time on a hydraulic bench. Total area reduction is 36-38%. The mandrels are made of tungsten carbide and are vanadium nitride coated.

Current Coating Operation:

Pre-treatment

[0085] Tubes are pre-treated with the following compositions and cold water in the following order.

- 1) EC 375 D (alkaline cleaner):, 170° F for 5 mins;
- 2) Cold Water Rinse (CWR);

- 3) 815 (Phosphoric acid pickle inhibited with Rodine 95): 180° F for 6 min;
- and
- 4) CWR.

Treatment

[0086] The pre-treated substrate is then contacted with an aqueous composition containing the acid-stable particles and one or more fluoroacids. The coating composition used in the process was Bonderite® NT-1, available from Henkel Surface Technologies, Madison Heights, MI. The concentration of the Bonderite® NT-1 is about 1% (v/v). The substrate is contacted with the composition at ambient temperature using three (3) fill-n drains, followed by a one (1) minute immersion. The pH of the composition is maintained at a pH from 4.8-5.2.

Post-treatment

[0087] The treated tubes are then post-treated with the following compositions and cold water rinse in the following order.

- 1) CWR
- 2) Fuch's Ecoform SYN 691 (naphthenic oil emulsion): 180° for 5 min.
- 3) Conveyor Oven: 320° F for 40 min.

[0088] One commercial advantage of using Bonderite® NT-1 over prior zinc phosphate and iron phosphate B 1030 compositions is the relative small amount of sludge waste generated in the composition tanks over time. In the past, the zinc phosphate sludge had to be shoveled out by hand. The iron phosphate sludge could be sprayed out with a garden hose every 3-4 months. Although the NT-1 bath does generate some sediment in after about 5 months, it is apparent that the bath-life has been significantly increased.

[0089] Another commercial advantage is that the bath need not be heated. The coating composition can be applied at ambient temperatures. Application temperatures include temperatures less than 28 °C, though the coating composition can be applied at still lower temperatures such as less than 25 °C. The stability of the coating compositions can be monitored by measuring the pH and a Hach colorimetric testing kit.

We Claim:

1. A process of forming on a metal substrate a composition prior to the substrate being cold worked, said process comprising a step of contacting the substrate with an aqueous composition comprising acid-stable particles and one or more fluoroacids, wherein the amount of the acid-stable particles in the coating composition is from 0.005% to 8% by weight on a dry weight basis.
2. The process of claim 1 wherein the contacting of the substrate with the aqueous composition is conducted for a time sufficient to form at least about 0.1 g/m² of a water insoluble conversion coating on the substrate.
3. The process of claim 1 wherein the contacting of the substrate with the aqueous composition is conducted for a time sufficient to form at least about 0.3 g/m² of a water insoluble conversion coating on the substrate.
4. The process of claim 1 wherein the contacting of the substrate with the aqueous composition is conducted for a time sufficient to form at least about 0.6 g/m² of a water insoluble conversion coating on the substrate.
5. The process of claim 1 wherein the contacting of the substrate with the aqueous composition is conducted for a time sufficient to form at least about 1.0 g/m² of a water insoluble conversion coating on the substrate.
6. The process of claim 1 wherein the substrate is a ferriferous metal substrate.
7. The process of claim 1 further comprising pre-treating the substrate with an alkaline cleaner and an acidic pickle solution.
8. The process of claim 7 wherein the substrate is a ferriferous metal substrate.

9. The process of claim 1 wherein the acid-stable particles are aluminum-modified silica particles, and the amount of the acid-stable particles in the coating composition is from 0.005% to 5% by weight on a dry weight basis.
10. The process of claim 1 wherein the acid-stable particles are nonaluminum-modified silica particles, and the amount of the acid-stable particles in the coating composition is from 0.005% to 5% by weight on a dry weight basis.
11. The process of claim 1 wherein the acid-stable particles are polymeric organic particles.
12. The process of claim 1 wherein the aqueous composition further comprises a product of the acid-stable particles and the one or more fluoroacids.
13. The process of claim 9 wherein the aluminum-modified particles comprise about 0.006% to about 1% by weight on a dry weight basis of the composition, and the aluminum-modified silica particles have a $\text{SiO}_2:\text{Al}_2\text{O}_3$ weight ratio from 80:1 to 240:1.
14. The process of claim 13 wherein the aluminum-modified silica particles have a $\text{SiO}_2:\text{Al}_2\text{O}_3$ weight ratio from 120:1 to 220:1.
15. The process of claim 10 wherein the nonaluminum-modified particles comprise about 0.006% to about 1% by weight on a dry weight basis of the composition.
16. The process of claim 1 wherein the composition has a pH from 4.5 to 5.5.
17. The process of claim 1 further comprising post-treating the substrate with a naphthenic oil emulsion at a temperature of at least 120 °C followed by heating the substrate at a temperature of at least 200 °C.

18. A process of forming on a metal substrate a composition prior to the substrate being cold worked, said process comprising a step of contacting the substrate with a series of compositions, the process comprising:

contacting the substrate with an alkaline cleaner followed by an acidic pickle solution to form a pre-treated substrate;

contacting the pre-treated substrate with an aqueous composition comprising acid-stable particles and one or more fluoroacids, wherein the amount of the acid-stable particles in the coating composition is from 0.005% to 8% by weight on a dry weight basis to form a treated substrate; and

contacting the treated substrate with a naphthenic oil emulsion at a temperature of at least 120 °C.

19. The process of claim 18 further comprising contacting the pre-treated substrate and the treated substrate to a water rinse.

20. The process of claim 18 wherein the acid-stable particles are aluminum-modified silica particles, and the amount of the acid-stable particles in the coating composition is from 0.005% to 5% by weight on a dry weight basis.

21. The process of claim 18 wherein the acid-stable particles are nonaluminum-modified silica particles, and the amount of the acid-stable particles in the coating composition is from 0.005% to 5% by weight on a dry weight basis.

22. The process of claim 21 wherein the nonaluminum-modified particles comprise about 0.006% to about 1% by weight on a dry weight basis of the composition.

23. The process of claim 18 wherein the composition has a pH from 4.5 to 5.5.

24. The process of claim 1 wherein the contacting of the substrate with the aqueous composition is conducted at a temperature of less than 28 °C.

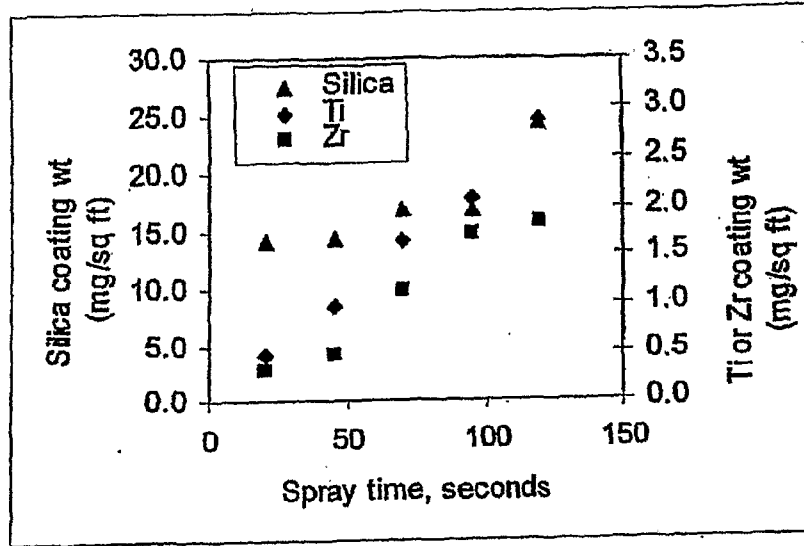


Figure 1

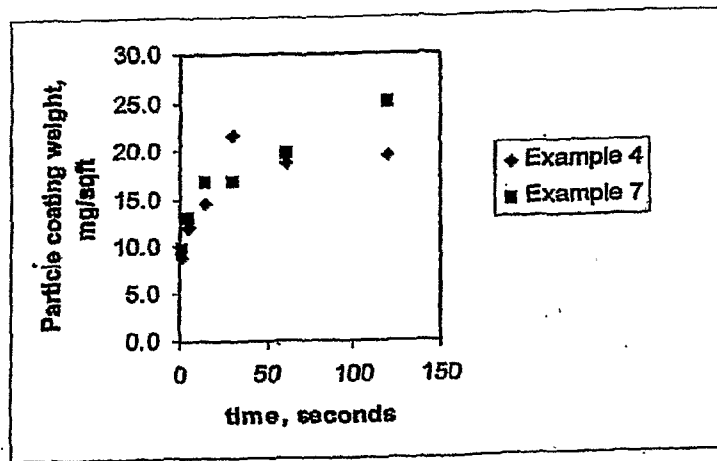


Figure 2

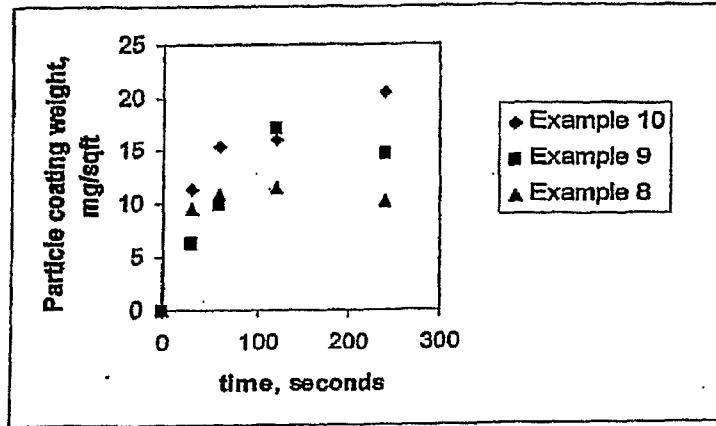




Figure 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2006/061781

A. CLASSIFICATION OF SUBJECT MATTER		
<i>C23C 22/00(2006.01)i</i>		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) IPC8 B05D 1/18, B21B 45/02, B32B 7/02, B32B 15/04, C10M 1/48, C10M 173/02, C23C 22/48.		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Korean Utility models and applications for Utility models since 1975. Japanese Utility models and applications for Utility models since 1975.		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) eKIPASS (KIPO internal) & keywords: coating composition, acid stable particle, fluoroacid, and similar terms.		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2004-063414 A2 (HENKEL KGAA) 29 July 2004	1 - 16
Y	See the abstract, page 3, line 14 - page 13, line 30 and examples.	17 - 24
Y	US 03984599 A (JAMES H. NORTON) 5 October 1976 See example 1.	17 - 24
Y	US 04374168 A (WESLEY J. WOJTOWICZ) 15 February 1983 See the abstract, and examples 1 - 3.	17 - 24
Y	US 05399274 A (R. STEVEN MARCUS) 21 March 1995 See the abstract, and example 1.	17 - 24
A	US 05281282 A (SHAWN E. DOLAN et al.) 25 January 1994 See the abstract, and claims 1 - 20.	1 - 24
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 12 APRIL 2007 (12.04.2007)		Date of mailing of the international search report 12 APRIL 2007 (12.04.2007)
Name and mailing address of the ISA/KR  Korean Intellectual Property Office 920 Dunsan-dong, Seo-gu, Daejeon 302-701, Republic of Korea Facsimile No. 82-42-472-7140		Authorized officer LEE, SUNG JOON Telephone No. 82-42-481-5530 

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2006/061781

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2004-063414 A2	29.07.2004	AU2003300475A1	10.08.2004
		AU2003302277A1	10.08.2004
		BR200317779A	22.11.2005
		CA2512591A1	29.07.2004
		CN1735713A	15.02.2006
		EP1590501A2	02.11.2005
		EP1592824A2	09.11.2005
		MXPA05006053A	16.08.2005
		RU2005125415A	10.02.2006
		US20040137246A1	15.07.2004
		US2006172064AA	03.08.2006
		US7063735BB	20.06.2006
		WO2004063291A2	29.07.2004
		US 03984599 A	5.10.1976
US 04374168 A	15.02.1983	CA1191058A1	30.07.1985
		DE3280178C0	28.06.1990
		EP0079187A2	18.05.1983
		JP58136699A2	13.08.1983
US 05399274 A	21.03.1995	NONE	
US 05281282 A	25.01.1994	AT154833E	15.07.1997
		AU2428795A1	29.11.1996
		AU3816893A1	08.11.1993
		BR9306172A	13.01.1998
		CA2132336C	21.10.2003
		CA2220419AA	14.11.1996
		CN1034683C	23.04.1997
		CN1067447C	20.06.2001
		CN1078271A	10.11.1993
		CN1151449A	11.06.1997
		DE69311802C0	31.07.1997
		DK633951T3	02.02.1998
		EP633951A1	18.01.1995
		ES2106330T3	01.11.1997
		HK1008057A1	30.04.1999
		JP7505447T2	15.06.1995
		KR1019950701012	20.02.1995
		MX9301865A1	01.11.1993
		NO943659A	24.11.1994
		NZ251233A	26.04.1996
		RU2125118C1	20.01.1999
		SG54220A1	16.11.1998
		US5356490A	18.10.1994
		US5534082A	09.07.1996
		US5769967A	23.06.1998
		WO9320260A1	14.10.1993
		WO9635745A1	14.11.1996
ZA9302181A	28.10.1993		