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PROCESS OF COATING

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This invention relates to the field of the chemical coating of metals. An object of the invention is the rendering of metallic surfaces resistant to corrosion. A further object of the invention is to form on metallic surfaces a chemical coating which resists corrosion when coated with a paint, lacquer, or enamel and provides a base coat to which the applied coatings adhere in a much firmer manner than they would to the bare metal.

Generally speaking, the invention comprises the use of solutions containing soluble hydrofluosilicic compounds with the addition of an oxidizing agent with or without accelerating agents. Hydrofluosilicic acid (H_2SiF_6) and soluble salts of this acid are comprised generally. Oxidizing agents such as hydrogen peroxide may be employed and accelerating agents such as nitrates may be used.

By the use of these materials surfaces of metals such as iron, steel, aluminum and zinc and alloys are rendered rust resistant and in many cases coatings are formed which serve as a rust resisting base for paints, lacquers, enamels, and other coating compositions.

The process comprises generally treatment of the metal surface by any of the ordinary methods. In the following examples which are given by way of illustration and not limitation the metallic surfaces were immersed in the solutions at a boiling temperature. The usual processing time was 5 minutes, although this may be decreased if desired. It is understood that the essential thing is to bring about a reaction between the surface of the metal and the solution and that the time, temperature, and other factors of operation may be varied considerably without departing from the scope of the invention. In the following examples 2" x 4" panels were employed in the usual case.

Example 1.—A sheet of aluminum was immersed in a 200 cc. solution to which had been added $\frac{1}{2}$ gram chromic acid, 3 cc. H_2SiF_6 . The metal was removed after 5 minutes at a boiling temperature and a hard, medium gray, very uniform coating had been produced upon the surface of the aluminum. When the same ingredients are used with the addition of 2 grams of sodium nitrate, a brown coating is obtained which is finer and softer.

Example 2.—The same conditions as in Example 1 were employed using a solution containing $\frac{1}{2}$ gram chromic acid and 5 grams manganese silicofluoride. A medium gray, very uniform, medium hard coating was obtained on the alumi-

num. When 2 grams of sodium nitrate is used with the other ingredients a harder, lighter, thinner coating is obtained.

Example 3.—Under the same conditions as in Example 1 a solution was employed containing $\frac{1}{2}$ gram chromic acid, and 5 grams sodium silicofluoride. The aluminum surface had a hard, thin, light gray coating. When 2 grams of sodium nitrate is used with the other ingredients the same result is obtained.

Example 4.—Under the same conditions as in Example 1 an aluminum sheet was treated with a solution containing 2 cc. of hydrogen peroxide and 3 cc. hydrofluosilicic acid. Coatings were obtained which may be described as white, under a fairly hard gray surface. When 2 grams of sodium nitrate is employed with the other ingredients a medium gray, fairly hard coating is obtained.

Example 5.—Under the same conditions as in Example 1 an aluminum object is immersed in a solution to which has been added 1 gram potassium permanganate and 3 cc. hydrofluosilicic acid. A red-purple iridescent fairly hard coating is obtained. When 2 grams of sodium nitrate is used with the same ingredients a dark purple, soft and dusty coating is obtained.

Example 6.—Under the same conditions as in the preceding examples a solution was employed using 2 grams potassium dichromate and 5 cc. hydrofluosilicic acid. A rather soft gray coating is obtained on the aluminum. When 2 grams of sodium nitrate is used with the other ingredients a hard, brown coating is obtained.

Example 7.—Under the same conditions as in the preceding examples a solution is used containing 2 grams sodium chromate with 3 cc. hydrofluosilicic acid. A dark gray, hard coating is obtained on the aluminum surface. When 2 grams of sodium nitrate is used together with the other ingredients a light brown, hard, thin coating is obtained.

Example 8.—Under the same conditions an aluminum surface is treated with a solution containing 2 grams chromium sulphate and 3 cc. hydrofluosilicic acid. There is obtained on the aluminum surface a soft green gray coating over a hard thin white. When 2 grams sodium nitrate is used together with the other ingredients, a thin, harder green coating is obtained.

Example 9.—The solution contained 2 grams chromic acid and 3 cc. hydrofluosilicic acid. The conditions were the same as in the preceding examples except an immersion time of 30 minutes

was taken. There was obtained on a steel surface a dark, gray, fairly hard coating.

Example 10.—The solution employed was made up by adding 1 gram chromic acid, $2\frac{1}{2}$ cc. H_2SiF_6 and 2 grams sodium nitrate. A black, adherent coating was obtained under a brown dust on a steel surface in 5 minutes.

Example 11.—Under the same conditions as in the preceding examples a steel object was processed in a solution containing 2 grams chromic acid, 5 grams manganese silicofluoride, $2\frac{1}{2}$ grams sodium nitrate for 1 to 5 minutes. There was obtained a black, adherent coating. The same results were obtained with the following ingredients in solution:

2 grams CrO_3 plus 5 grams FeSiF_6 plus $2\frac{1}{2}$ grams NaNO_3

2 gr. CrO_3 +5 gr. FeSiF_6 +2 gr. $\text{Mn}(\text{NO}_3)_2$

2 gr. CrO_3 +3 cc. $\text{Fe}_2(\text{SiF}_6)_3$ +2 gr. NaNO_3

10 cc. H_2SiF_6 +4 gr. K_2CrO_4 +2 gr. $\text{Mn}(\text{NO}_3)_2$

5 cc. H_2SiF_6 +2 gr. $\text{K}_2\text{Cr}_2\text{O}_7$ +2 gr. $\text{Mn}(\text{NO}_3)_2$

2 gr. $\text{Cr}_2(\text{SO}_4)_3$ +5 cc. H_2SiF_6 +2 gr. NaNO_3

Example 12.—Under the same conditions as in the preceding examples a steel object was processed in a solution containing 1 cc. H_2SiF_6 +3 gr. K_2SO_4 for 5 minutes. A like solution with 2 gr. NaNO_3 added gave the same rust proofing results as tested in the salt spray, both being an improvement over non-treated steel.

Example 13.—Other salts that may be substituted for K_2SO_4 in the combinations given in the example just above are:

NaCl

NaH_2PO_4

Na_2MoO_4

Na_2WO_4

Na_2SO_3

NaH_2PO_3

KClO_3

$\text{Na}_2\text{B}_4\text{O}_7$

Slight variations in proportions of the above listed combinations may be necessary, but improved rust proofing results can be obtained on steel from these examples.

Example 14.—To 200 cc. of water was added $2\frac{1}{2}$ cc. H_2SiF_6 and 1 cc. H_2SO_4 . A steel panel processed in this solution showed added corrosion resistance as compared to bare metal controls. Like results were obtained from this solution with 2 gr. NaNO_3 added thereto.

Example 15.—Other acids that may be substituted for H_2SO_4 under exact conditions as in the preceding examples are:

HCl

H_3PO_4

H_3PO_3

HClO_4

Molybdic acid

HNO_3

H_2SO_3

HClO_3

Boric acid

Tungstic acid

Slight variations in proportions may be necessary in the chemicals used in these examples, but added corrosion resistance is obtained from all of them.

Example 16.—Under the same conditions as in the preceding examples a steel object was processed in a solution containing $2\frac{1}{2}$ cc. H_2SiF_6 +1 cc. 30% H_2O_2 . A soft brown and black coating resulted in 5 minutes. A like solution containing 1 cc. H_2SiF_6 +1 cc. 30% H_2O_2 +2 gr. NaNO_3 produced a very uniform, adherent, light gray coating in 5 minutes. Both of these treatments gave exceptionally good salt spray test results.

Example 17.—Under the same conditions as in the preceding examples a steel object was processed in a solution containing $2\frac{1}{2}$ cc. H_2SiF_6 and 1 gr. KMnO_4 . A gray and brown coating re-

sulted in 5 minutes which was adherent under a loose top dust.

Example 18.—Under the same conditions as in the preceding examples a steel object was processed in a solution containing 1 cc. H_2SiF_6 + $2\frac{1}{2}$ gr. $\text{K}_2\text{S}_2\text{O}_8$. A thin iridescent coating resulted in 5 minutes but the addition of 2 grams NaNO_3 to this solution produced a dark gray coating.

Example 19.—Under the same conditions as the preceding examples a steel object was processed in a solution containing 6 gr. NaH_2PO_4 +6 gr. MnSiF_6 +4 gr. $\text{Mn}(\text{NO}_3)_2$ and a gray adherent coating resulted in 15 minutes at boiling temperature. Manganese dihydrogen phosphate may be substituted for the sodium phosphate in this example and FeSiF_6 or ZnSiF_6 may be substituted for the MnSiF_6 .

Example 20.—Under the same conditions as in the preceding examples a steel object was processed in a solution containing $2\frac{1}{2}$ cc. H_2SiF_6 and 2 gr. NaNO_3 . A very uniform soft gray coating resulted in 5 minutes. 5 gr. MnSiF_6 may be substituted for the H_2SiF_6 in this combination and very good corrosion resistance is shown from both treatments.

Example 21.—A 200 cc. solution containing 5 gr. MnSiF_6 +2 cc. 85% H_3PO_4 produced a good coating in 5 minutes. The addition of 2 grams NaNO_3 to this solution also produced a resistant coating in 5 minutes. In this example FeSiF_6 may be substituted for MnSiF_6 and $\text{Mn}(\text{NO}_3)_2$ may be substituted for the NaNO_3 .

In the following examples objects with a zinc surface were immersed in a boiling solution for 5 minutes.

Example 22.—1 gram CrO_3 plus 2 cc. H_2SiF_6 . A thin gray, fairly hard coating was obtained. When 2 grams of sodium nitrate is used with the other ingredients a coating is obtained which is gray with green tint, fairly hard and uniform. In this example if sodium nitrate is replaced by manganese nitrate or zinc nitrate similar results are obtained. When aluminum nitrate is employed in place of the sodium nitrate a coating is obtained which is hard, adherent and heavy gray.

Example 23.—2 grams chromium sulphate plus 2 cc. H_2SiF_6 . When 2 grams of sodium nitrate is used with the other ingredients a uniform, dark, dull, hard, adherent coating was obtained.

Example 24.—1 gram CrO_3 plus 1 gram KMnO_4 plus 2 cc. H_2SiF_6 . A hard gray coating under a soft purple one is obtained. When 2 grams of sodium nitrate is used with the other ingredients similar results are obtained.

Example 25.—1 gram CrO_3 plus 5 grams MnSiF_6 . A coating is obtained similar to that when using H_2SiF_6 in place of MnSiF_6 . When 2 grams sodium nitrate is employed with the other ingredients a green coating is obtained.

Example 26.—2 cc. H_2SiF_6 plus 2 grams sodium nitrate. A transparent, fairly hard, dark gray coating is obtained. When zinc nitrate is used in place of sodium nitrate, similar results are obtained.

Example 27.—1 gram chromic acid plus 1 gram of $\text{K}_2\text{S}_2\text{O}_8$ plus 1 cc. H_2SiF_6 . A hard gray mixed dark and light coating is obtained. When 2 grams sodium nitrate are used with the other ingredients a soft, dark green shiny finish is obtained.

In the above examples metals other than those specifically mentioned can be processed. Time, temperatures, proportions and ingredients can be varied well within the scope of the invention, the essence being the treatment of metals with solu-

tions containing the SiF_6 radical together with the use of oxidizing agents with or without accelerating agents.

The examples mentioned above include hydrogen-peroxide, nitric acid and nitrates, chromic acid, chromates and dichromates, permanganates, sulphurous acid and sulphites, chloric and perchloric acids and chlorates, molybdates, tungstates, and persulphates, which are recognized oxidizing agents, and other compatible oxidizing agents may be used. The oxidizing agent must, of course, be a compatible material, that is, it must be soluble in the solution and its oxidizing power must not be destroyed by the other ingredients in the solution before it has an opportunity to exert its oxidizing power in the chemical reaction that takes place at the surface of the work.

It has been found that acceleration is gained by adding to these solutions a soluble salt of a metal below the respective metal being treated in the electromotive series. This acceleration is apparent in quickening of processing time, more uniformity in the coating and in producing a heavier coating. In the case of treating an iron surface, salts of metals slightly above iron in the electromotive series may be used.

What I claim is:

1. A process of treating a surface of a metal included in the group consisting of iron, steel, zinc, aluminum and their alloys, which comprises subjecting said surfaces to the action of a heated solution containing the SiF_6 radical and one of the group consisting of chromic acid and nitric acid, and treating the metallic surface until a visible protective paint-holding coating is obtained thereon and then applying a coating of one of the group consisting of paints, lacquers and enamels.

2. A process of treating a surface of a metal included in the group consisting of iron, steel, zinc, aluminum and their alloys, which comprises subjecting said surfaces to the action of a heated solution containing a soluble hexavalent chromium compound and one of the group of H_2SiF_6 and soluble salts thereof, at least one of the aforesaid being added in the form of acid and continuing such action until a visible protective paint-holding coating is obtained upon the metal-

lic surface and thereafter applying a coating of one of the group consisting of paints, lacquers and enamels.

3. A process of treating a surface of a metal included in the group consisting of iron, steel, zinc, aluminum and their alloys, which comprises subjecting said surfaces to the action of a heated solution containing chromic acid and one of the group of H_2SiF_6 and soluble salts thereof, and continuing such action until a visible protective paint-holding coating is obtained upon the metallic surface and thereafter applying a coating of one of the group consisting of paints, lacquers and enamels.

4. A process which comprises treating a surface of a metal included in the group consisting of iron, steel, zinc, aluminum and their alloys with a heated solution containing the radical SiF_6 and nitric acid, and continuing such treatment until a visible, protective paint-holding coating is obtained upon the metallic surface and thereafter coating the surface with one of the group consisting of paints, lacquers and enamels.

5. A process of treating a surface of a metal included in the group consisting of iron, steel, zinc, aluminum and their alloys, which comprises subjecting said surfaces to the action of an acidulated heated solution containing as its chief active ingredients the SiF_6 radical and a compatible oxidizing agent, and treating the metallic surface until a visible protective paint-holding coating is obtained and thereafter applying to the metal surface a coating of one of the group consisting of paints, lacquers and enamels.

6. A process of treating a surface of a metal included in the group consisting of iron, steel, zinc, aluminum and their alloys, which comprises subjecting said surfaces to the action of an acidulated heated solution containing as its chief active ingredients the SiF_6 radical and a compatible oxidizing agent of the group consisting of nitrates and compounds of hexavalent chromium, and treating the metallic surface until a visible protective paint-holding coating is obtained and thereafter applying to the metal surface a coating of one of the group consisting of paints, lacquers and enamels.

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