May 28, 1963 J. J. KANTER 3,091,549
RESINOUS COATING OF SILICONIZED IRON
Filed May 18, 1960

Fig. 1

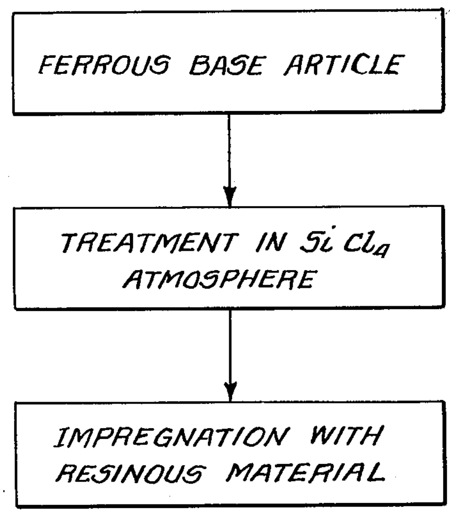
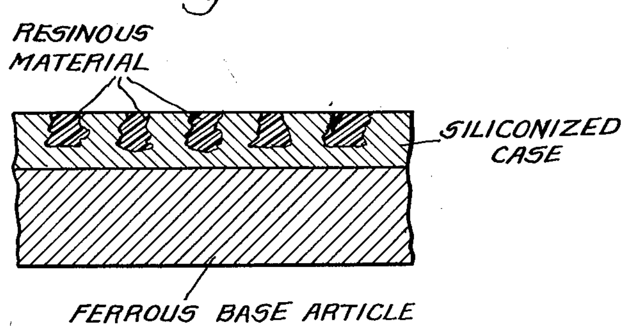


Fig. 2



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RESINOUS COATING OF SILICONIZED IRON

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This invention relates as indicated to corrosion resistant metals, and more particularly, to protecting ferrous base articles.

Metals have been protected in the past by applying to their surfaces materials having greater resistance to corrosion, chemical attack, weathering, than the metals themselves. For instance, tin, nickel, and chromium have been used to protect the metal surfaces. Well known chemical treatments, such as phosphating and siliconizing, have been employed to protect materials susceptible to corrosion.

Typical siliconizing processes are shown in the patents of Ihrig, 2,109,485; Henderson et al., 2,501,051, and Eckman, 2,897,093. In these processes the outer portion of the treated article is enriched in silicon. The ability of silicon to increase the resistance of a metal, or alloy, to corrosion, or to scaling at elevated temperatures, is well known. This is especially true of ferrous base articles. For example, it has been known for many years that steel containing silicon is highly resistant to the action of corrosive substances, particularly mineral acids, such as sulfuric acid. This characteristic of high-silicon steels has been employed commercially in apparatus required to resist chemical attack.

One disadvantage of the siliconizing processes in which the outer portion of the article is inoculated with silicon is the formation of a porous surface containing pits and voids in the surface of the treated article. The porous surface is susceptible to corrosion, chemical attack, and weathering. For this reason, siliconizing processes were developed in a direction to minimize, or reduce, the voids and pits formed during the siliconizing operation, such as shown in the Eckman patent supra. The results were, however, lessening of the depth and amount of porosity, without fully eliminating the disadvantages afforded.

It is, therefore, an object of the invention to provide a metal product having increased resistance against corrosion, rusting, or chemical attack. It is a further object of the invention to provide a protective coating which is firmly adherent and highly resistant to sustained action of many corrosive substances. Further objects and advantages of the invention will be apparent from a study of the description and the appended claims.

Briefly stated, the present invention relates to increasing the corrosion resistance of metal articles by contacting with a siliconizing reagent to inoculate the outer portion with silicon and form a porous surface, and then impregnating the porous surface with a synthetic resinous material. The invention is also related to a new article of manufacture comprising a metallic body having on the outer portion a high-silicon content and the interstices of the surface filled with a synthetic resinous material.

In the drawings:

FIGURE 1 is a flow sheet illustrating the process of the present invention; and

FIGURE 2 is a diagrammatical illustration in cross-section of an article of the present invention.

Metals of the invention have the fullest protection against corrosion or attack by chemicals. They possess a tough surface. Moreover, the synthetic resinous material forms an anti-friction layer making the article particularly applicable to uses as bushings, valves, sleeves, liners, washers, journals, and the like which are employed in corrosive atmospheres, or surroundings.

The siliconizing treatment may be carried out in several ways. According to the present understanding of the chemical mechanisms involved, each of the procedures forms silicon tetrachloride that reacts with the surface of the metal to form silicon, which inoculates the outer layer or portion of the article and forms a by-product chlorine gas.

According to one procedure, the articles receiving the siliconizing treatment are placed in a horizontal drum type retort. The retort is connected to a source of substantially dry inert gas, such as nitrogen, neon, or argon, which is introduced to displace the air. After the preliminary flushing, the flow of nitrogen, for instance, is reduced so as to be sufficient to make up for losses that may occur due to leakage. Then the retort is rotated and heat is applied, for example by electrical heating elements on the sides to raise the temperature to proper siliconizing levels. The temperatures are not critical, but generally best results are obtained at approximately 1850° F. for ordinarily low carbon steel with different temperatures for other alloys and non-ferrous metals.

After the siliconizing temperature is attained, the flow of the inert gas is shut off and silicon tetrachloride gas is introduced into the retort. This gas is generated by applying heat to a receptacle containing liquid silicon tetrachloride. Alternatively, the silicon tetrachloride may be introduced by a carrier gas which is bubbled through the silicon tetrachloride liquid and then conducted into the retort. After the retort has filled with the siliconizing reagent, with or without the presence of the carrier, the flow of the reagent is reduced to a slow, continuous ingress for the siliconizing process.

Ordinarily, the exposure time of the treated articles to the siliconizing atmosphere is from about 0.5 to about five hours. Usually satisfactory results are obtained within one to three hours.

After receiving the siliconizing treatment, the articles may be allowed to cool in the retort to room temperature, or may be removed to separate containers to lower temperatures for handling.

Heretofore, various processes were developed to reduce the contact of the by-product chlorine with the metal surface. For example, the Henderson Patent 2,501,051 introduces hydrogen into the treatment area. In the Eckman Patent 2,897,093, the article is tumbled with silicon carbide so that the chlorine reacts with the silicon carbide to reduce the amount of free chlorine present. In the present process, however, it may be desirable to keep the atmosphere surrounding the treated articles as corrosive as possible to increase the porosity by producing more, and larger, voids and pits on the surface, while at the same time inoculating the outer portions with the silicon. By increasing the voids and pits, the porosity is increased so that in the subsequent impregnation greater amounts of the resin may be introduced.

Other steps may be employed for increasing the porosity, or opening the pores and voids, preparatory to the impregnation. For example, after the siliconizing operation the articles may be reheated to high temperatures for a short period of time and then cooled in order to enlarge the openings at the surface of the articles. According to one procedure the articles are heated to 1400° F. for twenty minutes than furnace cooled overnight to open up the pores. In some instances the porosity may be increased by acid treatment, such as conventional etching procedures.

In accordance with the present invention the siliconized article which has been treated in the foregoing manner to produce a porous surface is impregnated with a resinous material. Satisfactory resinous materials which can be used in this connection are natural and synthetic resins such as polytetrafluoroethylene, known as "Teflon," polymerized acrylates, polymerized styrene, synthetic rubbers, rubber latex, and the like. Special preference is given to polytetrafluoroethylene because of its corrosion resistance.

The resinous material may be incorporated into the porous surface of the article by many known techniques, such as by flowing onto the surface of the article melted resinous material in its liquid phase, or by applying suspensions, dispersions, or emulsions. Alternatively, monomers may be introduced into the cavities and polymerized in situ.

According to one satisfactory procedure air is evacuated from the surface of the article by subatmospheric pressures. The resinous material is then applied to the evacuated surface in the form of a suspension in a vaporizable carrier liquid. The article is next placed under atmospheric pressures, or above, and the carrier liquid evaporated to leave the resin in the intersticial surface. This cycle may be repeated until the voids are substantially filled with the resin.

The following example is given by way of illustration of the process of the invention, but it is not to be taken as limiting the methods or techniques that may be employed:

Example

Two lubricated plug valve bodies were employed. The bodies were lapped to eliminate small nicks and to take down a small mound at the top of the seat where a grease ring had been located. After machining, the two plugs were siliconized. $SiCl_4$ was allowed to react with the plugs for one hour and ten minutes at about 1850° F. The control bar in the siliconizing furnace was cut and case depth determined to be .0235 inch. A corner of one plug was ground off and a rough measure of case depth was estimated at .021 inch.

The plugs were heated at 1400° F. for 20 minutes then furnace cooled overnight. This treatment successfully opened up the pores.

The siliconized plugs were re-centered and reground to their valve bodies. Dimensions at the top of the plugs were

Plug Number	Diameters		Δ	Depth of Case Removed
	Before Grinding	After Grinding		
1	2.814	2.803	.011	.0055
2	2.823	2.817	.006	.003

The grinding operation appeared to cover many of the surface pores.

The plugs were degreased by rinsing with trichloroethylene acetone, and then immersed in a dilute (5%) HF solution in order to increase the porosity. At first bubble evolution was slow, but when more surface area was exposed, evolution was faster. The plugs were etched in this manner until fast bubble evolution had proceeded for about one minute. They were then washed in a neutralizing rinse of dilute KCN, dried in an air stream, and placed in an oven overnight.

The plugs were allowed to cool to room temperature and then given an acetone rinse. They were then placed in vacuum for 30 minutes and impregnating emulsion (Teflon emulsion diluted with water to about 40% solids) was allowed to cover plugs as much as possible before completely removing vacuum. Covered with emulsion, the plugs were allowed to stand for 30 minutes under atmospheric pressures. After removal, the plugs were allowed to air dry, then were placed in a drying oven overnight.

Next they were heated to 700° F. for 10 minutes followed by an air cool. The excess Teflon was scraped from the plug seat surface with a wooden splint.

The impregnation operation was repeated for plug No. 2 for a total of 2 impregnation cycles. Plug No. 1 was given a total of 3 impregnation cycles.

A control piece from the control bar in the siliconizing operation was made, fired at 1400° F. for 20 minutes, surface ground, rinsed in acetone, dried in an oven and weighed. This piece was not etched with HF as the ground surface was quite porous. The control piece was impregnated three times, except that it was baked at 700° F. for only 5 minutes. It was weighed after each impregnation to determine the percent of case filled with Teflon. The case volume was measured at 0.1433 $cm.^3$ (i.e. 2.09 cm. x 1.172 cm. x .0586 cm.).

Impregnations	Weight, grms.	Total increase, gm.	Volume Teflon, $gm.^3$	Percent Teflon in case
0	3.7242			
1	3.7442	.0200	.0092	6.26
2	3.7488	.0246	.01135	7.9
3	3.7494	.0252	.0116	8.1

Other modes of applying the principle of the invention may be employed, change being made as regards the details described, provided the features stated in any of the following claims or the equivalent of such be employed.

I, therefore, particularly point out and distinctly claim as my invention:

1. The method for producing a corrosion resistant ferrous article which comprises contacting a ferrous base article with a siliconizing reagent containing silicon tetrachloride at elevated temperatures and for a time sufficient to inoculate the outer portions of said article with silicon and form a porous surface, and impregnating the silicon inoculated porous surface of the article with a synthetic resinous material.

2. The method of claim 1 in which said synthetic resinous material is polytetrafluoroethylene.

3. In a method for producing a corrosion resistant article the steps which comprise, inoculating at least one surface of a ferrous base article with silicon by contacting with a siliconizing reagent of silicon tetrachloride at elevated temperatures and for a time sufficient to form a porous structure in the surface of said silicon inoculated article, and impregnating the porous surface of said article with a synthetic resinous material.

4. The method of claim 3 in which said synthetic resinous material is polytetrafluoroethylene.

5. The method for producing a corrosion resistant ferrous article which comprises contacting a ferrous base article with a siliconizing reagent containing silicon tetrachloride at elevated temperatures and for a time sufficient to form said article with a high silicon case having a porous surface, and impregnating said porous surface of the article with a synthetic resinous material.

6. The method of claim 5 in which said synthetic resinous material is polytetrafluoroethylene.

7. As a new article of manufacture, a ferrous base article having a high silicon case and a porous surface, said porous surface impregnated with a synthetic resinous material.

8. The new article of claim 7 in which said synthetic resinous material is polytetrafluoroethylene.

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