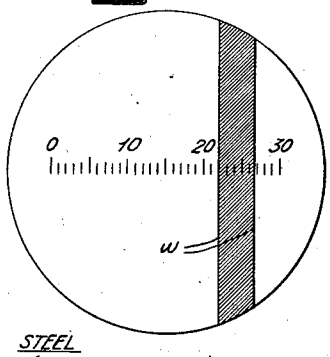
July 21, 1936. C. A. MARLIES ET AL 2,048,276

PLATED METAL HAVING CARBIDE SURFACE

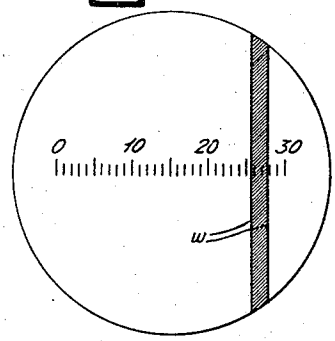
Filed April 21, 1932

Fig. 1



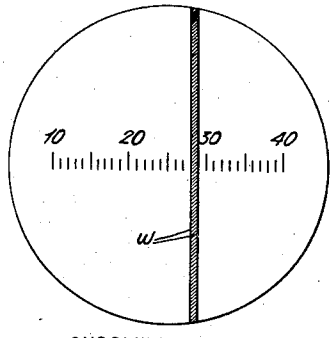
STEEL
w(SCRATCH WIDTH)= 0.0097 mm.
S(SCRATCH HARDNESS NUMBER)=550

Fig. 2



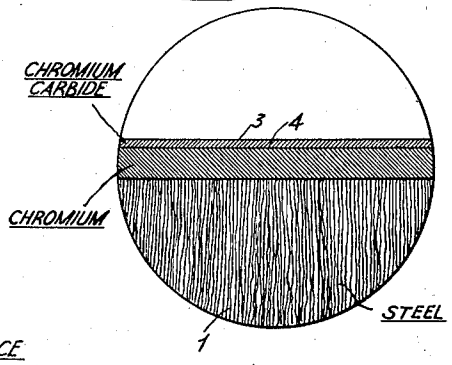
CHROMIUM PLATED STEEL
w = 0.0046 mm.
S = 2400

Fig. 3



CHROMIUM CARBIDE SURFACE
w = 0.0023 mm.
S = 9600

Fig. 4



INVENTOR
CHARLES A. MARLIES
GEORGE E. WHITE
BY Abraham S. Greenberg
ATTORNEY

Patented July 21, 1936 2,048,276

UNITED STATES PATENT OFFICE

2,048,276

PLATED METAL HAVING CARBIDE SURFACE

Charles A. Marlies and George E. White, New York, N. Y., assignors of one-half to Bruno S. Teschner, New York, N. Y.

Application April 21, 1932, Serial No. 606,736

8 Claims. (Cl. 148—31)

Our present invention relates to the carburizing of plated metallic surfaces, and more particularly to novel methods of producing carbided chromium, or tungsten, surfaces on chromium, or tungsten, plated metals, as well as to the novel products resulting from such methods.

The extreme hardness, stability at high temperatures, and corrosion-proof properties of chromium carbide render it an ideal surfacing material for metallic bodies which are subjected to severe temperature conditions, abrasion or chemical action. While chromium has been utilized as a surfacing material for such metallic bodies (as for example steel), a brief consideration of the comparative physical and chemical properties of chromium and chromium carbide readily demonstrates that the latter is superior. Thus, whereas chromium carbide has a hardness on Mohs' scale of 8.0 to 8.5, specific gravity of 6.7 and melting point of 2250° C., chromium has a hardness of 6.0, specific gravity of 7.1 and melting point of 1615° C. Again, whereas chromium oxidizes at high temperatures, and is chemically affected by hydrochloric acid, aqua regia, and sulphuric acid, chromium carbide is stable at high temperatures, and is unaffected by any of the aforementioned chemical agents.

Now, generally, according to our invention, chromium carbide, as distinct from the element chromium, is employed as a surfacing material for metallic bodies, such as steel, and specifically such a carbide is produced upon a layer of metallic chromium which has been plated upon the metallic body, it being pointed out that the present invention applies equally well to tungsten plated metallic bodies.

Hence, it may be stated that it is a prime object of this invention to utilize the existing chromium, or tungsten, plate of a metal body, as steel, for the production of a hard, carbide surface which is not only capable of protecting the underlying metal from abrasion, corrosion or chemical action, but is formed in an exceedingly uniform layer free from microscopic fissures, the uniformity not being impaired by sudden temperature variations.

Another important object of this invention is to provide chromium, or tungsten, plated steel which possesses a chromium, or tungsten, carbide surface capable of resisting to a greater extent than the uncarburized plate the action of concentrated acids and alkalies, including hydrochloric, nitric, and sulphuric acids, caustic soda and ammonia, and which, additionally, renders the steel readily capable of employment under such severe conditions of use as in connection with a great variety of equipment used in the chemical industries.

Still another object of this invention is to provide a carbided surface on a chromium, or tungsten, plated metallic body, such as steel or alloys thereof, which can be heated to a red heat and then quenched, without cracking, distortion, or loss of chemical resistivity.

Another object of our invention is to provide a great variety of methods for producing carbided surfaces on chromium, or tungsten, plated steel, the methods basically involving the treatment of the plated steel, at an elevated temperature, with a carbonaceous substance, the latter being one of a genus including such widely different materials as molten cyanide baths including, as is well known in the art, other fused salts, asphalt, sawdust, mixtures of sand and calcium carbide, case-hardening mixtures, charcoal, and mixtures of gaseous hydrocarbons, such as vaporized benzol, ethylene, acetylene, natural gas, or illuminating gas.

Still another object of the present invention is to provide a chromium carbide surface on an electroplate of chromium upon steel which surface is characterized by having a surface hardness of the Brinell scale of the order of four times as great as that of the chromium plate itself, and of the order of ten times as great as that of the steel, the surface being produced by carburization of the surface of the plate.

Still other objects of the invention are to improve the utility of chromium, or tungsten, plated metallic bodies, as steel, by providing various methods of carburizing the plated surface, the methods not only being commercially practicable, but reliable in operation.

In the following description modes of putting this invention into practice will be disclosed, but we do not wish to be understood as confining the invention to the specific mode of operation, or the ingredients set forth, as many variations may be introduced, well within the spirit of this invention as defined in the claims succeeding the description.

In the drawing,

Fig. 1 shows a photomicrograph of the result of a scratch hardness test on a steel surface,

Fig. 2 shows a similar photograph of a similar test on the surface of chromium plated steel,

Fig. 3 shows the result of a similar test on a surface embodying the invention,

Fig. 4 illustrates a photomicrograph of a section of the specimen shown in Fig. 3.

Referring, now, to the accompanying drawing wherein like reference characters in the different figures designate similar elements, there is shown in Fig. 4 a representation of a photomicrograph of an embodiment of the present invention. The figure illustrates a section of a ferrous body 1, such as steel, which is provided with a chromium plate 2, the latter having its exposed surface carburized, as shown at 3. Examination of this section under the microscope indicated a very uniform carbide coat of the order of 0.002 mm., in thickness, the chromium plate being of the order of 0.006 mm., in thickness. The bond 4 between the two coats 2 and 3 is not only excellent, no voids whatever being observed at a visual magnification of 350, the surface being highly uniform. The adhering quality of the carbide film 3 is well shown by the possibility of cutting and polishing the specimen without tearing such a thin film completely away from the adjacent chromium layer 2.

Chromium plated steel articles may be treated under a variety of conditions to produce the layer of chromium carbide on the surface of the chromium. One possible method is described hereinafter, the carbide surfaces formed being uniform and extremely fine grained. Not only are the surfaces hard and uniform, resisting to a substantial extent the action of concentrated acids and alkalies, but they can be heated to a red heat and then quenched, without cracking, distortion, or loss of resistance to chemical action. Generally, the method employed in producing the novel product shown in Fig. 4 consists in subjecting the plated surface, at an elevated temperature, to the action of a fluid carbonaceous material.

Specifically, the metallic body, as steel, is first plated with a metal of a group including chromium and tungsten. The plating may be effected electrolytically in any well known manner. Those skilled in the art are well aware of the technique of chromium plating, for example, and therefore it is not believed necessary to describe the plating details, except to point out that the plating is carried out until the desired thickness of chromium, or tungsten, is deposited on the steel body, preferably at a temperature of about 65° C. in order to produce a coat of minimum porosity and minimum content of occluded gas. The chromium plated steel body, when ready for carburization, is placed in a carburizing vessel.

When carburization is to be effected by means of gaseous hydrocarbon the vessel utilized should permit ready ingress and egress of these gases. The temperature of the chamber is maintained at about 800° C., for about twenty minutes as a stream of gaseous hydrocarbon, such as illuminating gas with or without the enrichment of benzol vapor or other vaporized liquid hydrocarbons; ethylene; acetylene; natural gas, is passed over the plated body. Additionally, the plated surface may be freed of occluded gases, prior to the carburization, by heating the plated body in vacuo to 300° C., for about thirty minutes. This pre-treatment, while not essential, may improve the carbide coating if the plate contains much occluded gas. What is important during the carburization, is that a continuous stream of the gaseous hydrocarbon be passed over the plated surface so as to ensure the presence of sufficient acetylene. It is for this reason that methods affording no continuous supply of gaseous hydrocarbon result in carbide surfaces showing little improvement in surface hardness.

The most uniform and satisfactory surfaces are produced by the use of fluid carburizing agents. This condition is realized in the gaseous carburizing process just described, or in carburization by means of fused baths containing cyanides, or other carbon-bearing materials.

It is also pointed out that carburization in a case-hardening furnace may be employed. In such a case the plated article may be case-hardened in any usual manner well known to those skilled in the art. The case-hardening mixtures which may be sawdust, wood charcoal, mixtures of silica sand and calcium carbide, molten baths containing cyanides, or combinations of these.

Carbide surfaces are secured, when using the first of said aforementioned methods, which resist the sudden temperature changes occurring in quenching, as well as the action of concentrated hydrochloric acid. Proof of the formation of the chromium carbide surface is obtained qualitatively by the change in color, the miscroscopic structure, and the reaction toward concentrated hydrochloric acid; quantitatively by the marked increase in surface hardness over that of the original chromium plate.

Figs. 1, 2 and 3 illustrate the results of comparative surface hardness tests on the surfaces of the steel body, the chromium plate and the chromium carbide respectively. Thus, in Fig. 1 each division of the microscope scale represents 0.0023 mm. The shaded area ω represents the scratch made with a diamond point pressed against the surface of the steel by a known weight. This scratch test is well known to those skilled in the art, and is employed as a measure of surface hardness of thin metallic coats. The width of the scratch produced by the diamond point was 0.0097 mm., under a 20 gram load. The value S, representing the scratch hardness number, can be shown to be obtainable by the expression:

$$S=\frac{8L}{\pi\omega^2}, \text{ where L=the load in kg.}$$

S, for the untreated steel surface, has a number of 550. Fig. 2 shows the width of the scratch produced on the chromium plate surface under similar conditions. The value of ω is 0.0046 mm., while S in this case is 2400. Fig. 3 clearly demonstrates the relative hardness of the chromium carbide surface as produced by the first of the herein named methods. The value of ω is 0.0023 mm., under the same conditions; while, S has been greatly increased to 9600, a magnitude of the order of twenty times that of the untreated steel surface and four times that of the chromium surface. It is to be noted however, that S may have a value (depending on the carburization method employed) ranging between six and twenty times as great as that of an untreated steel surface.

The characteristics of the surface shown in Fig. 3 may be defined as being purple in color, the range of colors possible being greenish-blue to black; it is further iridescent in thin layers; extremely fine grained; appearing to have a cellular network which extends across scratches of the diamond point. It is pointed out that while the diamond point indents the surface, it does not remove the surface structure as described above. To demonstrate still further the magnitude of the surface hardness of the present product, reference is made to the following materials

for results of scratch tests, performed under similar conditions as those already described:

Brass_____S=150;
Brinell hardness number= 45 to 70
Monel metal_____S=320;
Brinell hardness number=110 to 300
Nickel_____S=380;
Brinell hardness number= 90 to 300

The above Brinell hardness numbers are the range of tabulated values found in the literature. It has been shown that a linear factor gives the relationship between scratch hardness and standard Brinell hardness (a measure of hardness in the mass). This linear factor in the present case is approximately 0.4. Using this approximate relationship the apparent Brinell hardness number of the chromium carbide surface of Fig. 3 ranges between 2000 and 4000.

While we have described several methods of, and products resulting from, carburization of chromium and tungsten plated metallic bodies, it is to be clearly understood that the present invention is in no way limited to the aforegoing specific ingredients, temperatures and other quantities, but that the invention is rather to be construed in the light of the following claims, since many other modifications will readily occur to those skilled in the art from the present disclosure.

What we claim is:

1. As a new article of manufacture, a metallic body having a thin layer consisting only of chromium carbide on, and adhering to, a chromium plated surface of the body.

2. As a new article of manufacture, a metal body having only a superficial layer of tungsten carbide on, and adhering to, a tungsten plated surface of the body.

3. As a novel product, a ferrous body, a surface of the body being plated with a layer of a single metal of the group including chromium and tungsten, the exposed surface of said layer being carburized.

4. As a novel product, a metallic body, a surface of the body being plated with a layer of a single metal of the group including chromium and tungsten, the exposed surface of said layer being carburized, said surface being carburized to a depth such that its surface hardness is of the order of four times that of the uncarburized plate surface.

5. An article of manufacture consisting of a metallic foundation body, a chromium plate deposit provided on the entire exposed face of said body, the metal of said body being other than the metals of the group including chromium, and a skin of surfacing material of substantially less thickness than the thickness of the plate deposit on said plate which is extremely harder than either the plate or said body, said material consisting solely of chromium carbide.

6. An article of manufacture consisting of a metallic foundation body, a chromium plate deposit provided on the entire exposed face of said body, the metal of said body being other than the metals of the group including chromium, and a skin of surfacing material of substantially less thickness than the thickness of the plate deposit on said plate which is extremely harder than either the plate or said body, said material consisting solely of chromium carbide, said skin being characterized by the fact that it is formed in a uniform layer free from microscopic fissures, the uniformity being unimpaired by sudden temperature variations.

7. An article of manufacture consisting of a metallic foundation body; a plate deposit, consisting substantially of a metal of the group including chromium and tungsten, provided on a surface of the body; the composition of said body being free of said metal; a skin of surfacing material, of substantially less thickness than the thickness of said plate deposit, on said plate; said material consisting substantially of the carbide of said metal.

8. As an article of manufacture, a metallic foundation body, a surface of the body being plated with a layer of a metal of the group including chromium and tungsten, the exposed surface of the said layer being a carbonaceous compound of said metal, and said surface being characterized by a coloration which is in marked contrast to that of the plated layer.

CHARLES A. MARLIES.
GEORGE E. WHITE.