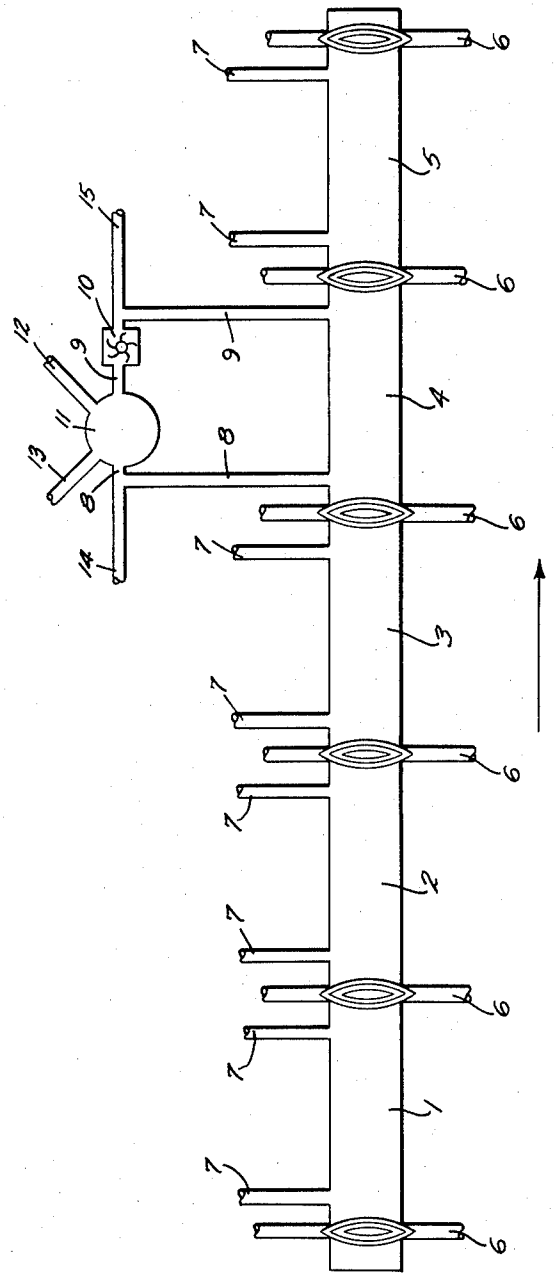
Oct. 14, 1958 R. NOWAK ET AL 2,856,312

TREATING METAL SURFACES

Filed June 30, 1954



INVENTORS
Rudolf Nowak and Ernst Hasse
BY Michael S. Striker
ATTORNEY

United States Patent Office 2,856,312
Patented Oct. 14, 1958

2,856,312

TREATING METAL SURFACES

Rudolf Nowak, Frankfurt am Main, and Ernst Hasse, Dusseldorf, Germany

Application June 30, 1954, Serial No. 440,408

Claims priority, application Germany July 3, 1953

18 Claims. (Cl. 117—50)

The present invention relates to the treatment of metal surfaces, and more particularly to methods of improving the surface characteristics of metal articles by treatment thereof in a gaseous atmosphere.

In the following discussion, the term "base metal" refers to the metal of the metal article or workpiece to be treated for improvement of the surface, and "diffusion element" refers to those metals or non-metals which become incorporated into the surface of the metal article for the improvement of the surface.

There are known surface improving processes where by thermal decomposition of easily decomposable compounds such as carbonyls, iodides and aluminum monofluoride, protective substances are deposited on the surface of the workpiece to be improved. These protective substances diffuse more or less rapidly into the base metal, depending upon the particular alloying affinity.

Another, and by far larger group of processes, is not based upon the thermal decomposition of easily decomposable compounds but are heterogeneous chemical replacement reactions. In these processes the diffusion element is brought onto the surface of the workpiece to be improved in the form of a gaseous chemical compound at high temperature. This gaseous chemical compound reacts with the base metal by way of chemical replacement. Thus the diffusion element diffuses into the surface of the workpiece, while an equivalent part of the base metal leaves the surface of the workpiece as a gaseous chemical compound and is drawn-off.

In most of these latter processes, almost exclusively halogen compounds of the diffusion elements are applied in a non-oxidizing atmosphere.

In other processes, hydrogen or inert carrier gases and hydrogen, are added to the gaseous compounds of the diffusion element. This leads to a deposition of the diffusion element on the base metal. This diffusion element simultaneously or subsequently is permitted to diffuse into the base metal. Catalysts, such as $FeCl_3$, $AlCl_3$, and $MgCl_2$, may or may not be added. With these latter processes, previously prepared gaseous halogenides of the diffusion elements can be used. The desired halogenides of the diffusion elements can also be produced by the reaction between the halogen or any of the halogenide vapors and the metallic or non-metallic original substances. The workpieces can either be put into the metallic or non-metallic original substance whereupon gaseous halogen or the vapors of halogenides are brought to action, or the desired halogenide of the diffusion element can be produced in a special chamber and subsequently used for diffusion treatment in a second chamber where the workpiece is located.

In connection with these replacement reactions, a gaseous waste product (the halogenide of the base metal), is always produced. This undesired reaction product is in some cases continuously removed (e. g. by way of condensation) from the reaction gases being circulated, and the consumed amount of the halogenide of the diffusion element is replaced in the circuit from the outside.

A chemical regeneration of the waste gases produced by the diffusion treatment does not take place here. Reaction periods of several hours are required to produce satisfactory improved surfaces with the above-described processes. This relatively long period of time is the reason why these processes have not been commercially applied on a large scale and that to date no one has been able to develop an economically operating continuous process during which the waste gases are continuously regenerated.

Also, it has been proposed to produce a surface improvement with halogenide vapors of the corresponding diffusion elements mixed with an exactly dosed addition of free halogen. It is true that with this process greatly improved surfaces can be obtained in relatively short periods of time. But it has also been learned that this is possible only if the velocity of the flowing reaction gas mixture is kept very low.

In the case of flat surfaces, the low flowing velocity of the reaction gas mixture is of no importance. With profiled workpieces, however (e. g. screws), higher gas velocities are required to obtain a sufficiently fast gas exchange in the indentations of the surface.

It is therefore a primary object of the present invention to provide a method of treating metal surfaces to improve the same whereby all of the above enumerated disadvantages of the known methods are eliminated.

It is still another object of the present invention to provide a continuous process of treating metal surfaces whereby waste gases formed during the process of treating the metal surfaces are continually regenerated for the further treatment of metal surfaces.

It is another object of the present invention to provide a rapid process for the treatment of metal surfaces to improve the same whereby the time of treatment is considerably shortened while still being able to continuously regenerate the waste gases for further treatment of metal surfaces.

It is yet another object of the present invention to provide a method of treating metal surfaces to improve the same by reaction of the metal surfaces with gases whereby a sufficient velocity of the gases is utilized so that profiled workpieces such as screws and the like can be treated.

Other objects and advantages of the present invention will be apparent from a further reading of the specification and of the appended claims.

With the above objects in view, the present invention mainly comprises a process of treating the surface of metals utilizing the step of subjecting the surface of the metal to be treated to vapors of a subhalogenide of an element adapted to react by heterogeneous chemical replacement with the metal so that the element replaces the metal in the surface and the metal replaces the element in the subhalogenide.

The present invention is based upon the surprising discovery that much improved surfaces can be obtained in a very short time through the application of high reaction gas velocities, if in the diffusion treatment subhalogenides of the diffusion elements are used. The reaction gases are such subhalogenides which react with the base metal by heterogeneous chemical replacement reaction.

The term "subhalogenide" as used throughout the specification and claims is meant to denote a halogen compound of the diffusion element which possesses less halogen atoms than that corresponding to the lowest valence of the diffusion element. For example, the lowest valence of tin is Sn^{++} so that the subchloride of tin would be SnCl. In addition, the term "subhalogenides" is meant to include mono-halogenides of those elements which in their lowest form are monovalent. The following are examples of subhalogenides which may be used accord-

ing to the present invention, the scope of the invention not however being limited to the specific subhalogenides mentioned: SiCl, $SiCl_2$, AlCl, TiF, ZnBr, SbCl, CCl_2, SnCl, BF, CrCl, CuCl, CuI, CuBr, CuF.

As is generally known, subhalogenides result from the reaction between halogens or halogenide vapors and an excess of metal or non-metal.

According to the present invention, neither a halogen nor an arbitrarily chosen halogenide vapor need be used to produce the subhalogenides. The required subhalogenides are produced according to a preferred embodiment of the present invention by reacting the halogenide of the basic metal (being a product of the heterogeneous chemical replacement reaction) with the diffusion element or an original substance containing the diffusion element. In this way, a continuous chemical regeneration of the gaseous products of the diffusion treatment (preferably within the circuit) is made possible. Thus the reaction waste gases, having left the treated workpiece, are brought in contact with the diffusion element introduced from the outside, and the formed subhalogenide vapors are led back for the diffusion treatment.

As mentioned above, this procedure permits the use of any desired high velocity of the reaction gas flow with surprisingly short periods of treatment.

Perfectly improved surfaces can be produced also on profiled workpieces within a few minutes. This is in contrast to all processes of this kind presently known.

The present invention which may be utilized for the treatment of any metal surface of any metal object is particularly adapted for the treatment of iron or iron alloy, e. g. steel objects and more particularly to iron and steel workpieces.

The continuous process of the present invention may start with the treatment of metal surface, e. g. iron, with a subhalogenide, e. g. AlCl, whereby the aluminum enters the surface of the iron object and ferrous chloride is formed; regenerating AlCl from the formed ferrous chloride by reaction of the ferrous chloride with aluminum or aluminum containing substances; and utilizing the thus formed AlCl, in vapor form, for the treatment of additional iron objects.

Alternatively, it is possible to carry out the process without ever forming any of the subhalogenide outside of the closed reaction circuit. For example, an iron object may be treated with vapors of $AlCl_3$, whereby the Al enters the surface of the iron object and ferrous chloride is formed. The thus formed ferrous chloride is then reacted with aluminum or an aluminum-containing substance to form AlCl vapors, the formed AlCl vapors then being used for the treatment of additional iron objects, and the reaction continuing in the closed circuit.

It has further proved advisable in connection with the present invention to add to the reaction gases catalysts which increase the reaction speeds. Such catalysts are, preferably full halogenides, for example, ferric chloride ($FeCl_3$), ferrous chloride ($FeCl_2$), the chlorides of tin ($SnCl_2$ and $SnCl_4$), aluminum chloride ($AlCl_3$), aluminum bromide ($AlBr_3$), boric fluoride (BF_3), boric chloride (BCl_3), cupric chloride ($CuCl_2$), and magnesium chloride ($MgCl_2$). It is not advisable to use compounds of the base metal in this connection.

If several diffusion elements are to diffuse jointly, the reaction gases must be brought to reaction with a mixture or with chemical compounds of the diffusion elements in the regeneration process.

It is preferable according to the present invention to activate the surface of the metal to be treated for chemical treatment by first oxidizing and subsequently reducing the surface. This increases the ability of the surface for heterogeneous chemical replacement reaction on which the diffusion of the diffusion element into the surface is based, and it achieves an evenness in the diffusion zone to be created which extends over the entire surface of the workpiece.

The novel features which are considered as characteristic for the invention are set forth in particular in the appended claims. The invention itself, however, both as to its construction and its method of operation, together with additional objects and advantages thereof, will be best understood from the following description of specific embodiments when read in connection with the accompanying drawings, in which the drawing schematically illustrates the device for carrying out the process of the present invention.

Referring more particularly to the drawing, the workpieces to be treated pass through consecutive treatment chambers. The workpieces first pass through the heating chamber **1**, then through the oxidation chamber **2**, subsequently through the reduction chamber **3**, thereupon through the diffusion chamber **4** and finally through the cooling chamber **5**. In order to isolate the different treatment gases in the various chambers, gas barriers **6** are placed between the individual chambers and are also located at both ends of the treatment apparatus. In addition, every treatment chamber has pipe lines **7** to introduce and remove the treatment gases.

The diffusion chamber **4** is connected with the regeneration chamber **11** by pipe lines **8** and **9**. Also a rotary blower **10** is installed in this circuit. Pipe line **12** serves as a supply line for the diffusion substance into the regeneration chamber **11**. Waste products of the regeneration can escape through pipe line **13**. Pipe lines **14** and **15** are connected to pipe lines **8** and **9** respectively and are used to fill or empty the system as well as for the introduction of catalysts.

The individual treatment chambers can be heated. This arrangement is such that any desired temperature can be maintained independently in the individual chambers. The temperatures in the pipe lines can be regulated in the same manner. The workpieces to be treated are processed in the direction of the arrow through the individual treatment chambers **1** through **5**. In chamber **1** they are heated up to the reaction temperature. In chamber **2** the surface is oxidized (e. g. with air). In chamber **3** it is reduced and activated (e. g. with hydrogen). In chamber **4** the workpieces come in contact with the reaction gases, whereupon the diffusion takes place. In chamber **5** they are cooled to a desired temperature.

The rotary blower **10** forces the reaction gases through the circuit from the diffusion chamber **4** through the pipe line **8**, through the regeneration chamber **11**, through pipe line **9**, and finally back into the diffusion chamber **4**. As the gases pass through the regeneration chamber **11** they react with the diffusion substance which is fed into the regeneration chamber **11** through pipe line **12**. The waste products of the regeneration in the regeneration chamber **11** are withdrawn through pipe line **13**.

The units can be constructed and arranged in various ways. The treatment apparatus **1** to **5** and the regeneration chamber **11** can, for example, be arranged horizontally, vertically, or diagonally. They can have the form of rotary kilns, retort furnaces, towers, etc. The flow-direction of the workpieces can be in the same flow-direction as the reaction gases. It can also be in the opposite direction or in any combination, continuously or discontinuously. These details will always be determined by the nature of the workpiece to be treated, by the size of the unit and other factors.

The following examples are given as illustrative of the process of the present invention and specific embodiments thereof, the scope of the invention not however being limited to the details of the examples.

Example 1

Sheet steel plates as used for the production of radiator sections should be siliconized as a protection against corrosion.

For this purpose the workpieces pass, one after the other, through the various treatment chambers. Chamber

1 is heated up to reaction temperature, approximately 950° C. The transit speed is regulated so that the plates remain in the diffusion chamber approximately 3 minutes. The pipe lines and the regeneration chamber are also maintained at a temperature of approximately 950° C.

Technical silicon or ferro-silicon, in powder form, is fed into the regeneration chamber as the diffusion substance. When starting the unit a mixture of 95% silicon tetrachloride vapor and 5% aluminum chloride vapor is introduced through pipe line **14** into the circuit. This vapor mixture is circulated in the system by means of the blower. Three percent aluminum chloride vapor is maintained in the system continuously through pipe line **15**. The silicon tetrachloride reacts in the diffusion chamber with the surface of the plates whereby silicon diffuses into the surface of the plates and ferrous chloride vapor is produced as a reaction product. The reaction gases flow from the diffusion chamber through the pipe line **8** into the regeneration chamber in which the ferrous chloride is regenerated by the silicon or ferro-silicon to subchlorides of silicon. Iron which is deposited in powder form is removed through pipe line **13**. The formed silicon subchlorides are then passed into the diffusion chamber **4** for reaction with additional steel plates, the ferrous chloride formed in the diffusion chamber being regenerated in the regeneration chamber into the subchlorides of silicon and the reaction continuing in this manner. The siliconized plates then are passed from the diffusion chamber **4** through the cooling chamber **5** to the outside.

Example 2

Grate bars of cast-iron or steel are to be made resistant to scaling by means of aluminum and silicon in a diffusion treatment.

For this purpose the grate bars pass one after the other through the various treatment chambers. They are heated in chamber **1** to a reaction temperature of approximately 1000° C. The transit speed of the grate bars is regulated in such manner that the bars remain in the diffusion chamber for about 4 to 5 minutes. The temperatures in the pipe lines and the regeneration chamber are also maintained at about 1000° C.

A mixture of 70% technical silicon and 30% technical aluminum in powder form is introduced into the regeneration chamber as the diffusion substance. When starting the unit, silicon tetrachloride vapor is fed through pipe line **14** into the circuit. This vapor mixture is circulated in the system by means of the blower. The silicon tetrachloride reacts in the diffusion chamber with the surface of the transient grate bars whereby silicon and aluminum diffuse into the surface of the grate bars and ferrous chloride vapor is produced as a reaction product. The reaction gases pass from the diffusion chamber through pipe line **8** into the regeneration chamber in which the ferrous chloride is regenerated by the silicon and aluminum to subchlorides of silicon and aluminum. Iron which is deposited in powder form is removed through pipe line **13**. The formed subchlorides of silicon and aluminum are then passed into the reaction chamber wherein they react with additional iron or steel bars, the ferrous chloride formed during the reaction being regenerated in the regeneration chamber to subchlorides of silicon and aluminum and the subchlorides passing into the reaction chamber for the treatment of additional iron or steel bars. The siliconized grate bars pass from the diffusion chamber through the cooling chamber to the outside.

Example 3

Electrical heating wire made of molybdenum is to be made resistant to scaling.

For this purpose the molybdenum wire is drawn through the various treatment chambers. It is heated in chamber **1** to the reaction temperature of approximately 1250° C. The transit speed of the wire is regulated in such a manner so that—depending upon the desired thickness of the protective layer—the wire remains in the diffusion chamber for about 3 to 7 minutes. The temperatures in the pipe lines and the regeneration chamber are also maintained at about 1250° C.

Technical titanium or a highly concentrated ferrotitanium in powder form is introduced into the regeneration chamber as diffusion substances. When starting the unit, a mixture consisting of 96% titanium tetrachloride and 4% boric fluoride is fed through pipe line **14** into the circuit. This vapor mixture is circulated in the circuit by means of the blower through pipe line **15**. Approximately 2% boric fluoride vapor is maintained in the system continuously. The titanium tetrachloride reacts in the diffusion chamber with the surface of the molybdenum wire, whereby the titanium diffuses into the surface of the wire and molybdenum fluorides form as gaseous reaction products. The reaction gases flow from the diffusion chamber through pipe line **8** into the regeneration chamber in which the molybdenum fluoride is regenerated by the titanium or ferrotitanium to subfluorides of titanium. In this connection, molybdenum powder is deposited and removed through pipe line **13**. The formed subfluorides of titanium are passed into the diffusion chamber wherein they react with additional heating wire and the process is thus continued. The titanium-coated molybdenum wire passes through the cooling chamber to the outside.

Example 4

Various objects out of iron or steel, such as floor or hanging lamps, chandeliers, decorated iron gates and fences, pieces of jewelry, etc., in short, objects of iron or steel the surface of which is to appear as gold-plated and to be corrosion-resistant, must be treated as follows:

The workpieces pass, one after the other, through the various treatment chambers. In chamber **1** they are heated to a reaction temperature of approximately 870° C. The transit speed of the workpieces is regulated in such a manner so that the workpieces remain in the diffusion chamber **4** approximately 10 minutes. The temperature in the pipe line and the regeneration chamber are also maintained at approximately 870°–900° C.

A mixture of 80% copper and 20% aluminum in powder form is introduced into the regeneration chamber as the diffusion substance. When starting the unit an aluminum bromide vapor is fed through pipe line **14** into the circuit. This vapor is circulated in the system by means of the blower. The aluminum bromide reacts in the diffusion chamber with the surface of the objects whereby aluminum diffuses into the surface of the objects and ferrous bromide vapor is formed as a reaction product. The reaction gases pass from the diffusion chamber through pipe line **8** into the regeneration chamber in which the ferrous bromide is regenerated by the metal powders to subbromides of aluminum and copper. By this process iron is deposited in powder form and is removed through pipe line **13**. The subbromides aluminum and copper are then passed into the diffusion chamber **4** wherein they react with the iron or steel objects, the ferrous bromide vapors formed in the diffusion chamber being reconverted in the regeneration chamber **11** into the subbromides of aluminum and copper which subbromides are subsequently passed into the diffusion chamber wherein they react with additional iron and steel objects. The objects thus treated pass from the diffusion chamber through the cooling chamber to the outside. The gold-colored mat surface can be polished.

Without further analysis, the following will so fully reveal the gist of the present invention that others can by applying the current knowledge readily adapt it for various applications without omitting features that, from the standpoint of prior art, fairly constitute essential characteristics of the generic or specific aspects of this invention and, therefore, such adaptations should and are

intended to be comprehended within the meaning and range of equivalence of the following claims:

What is claimed as new and desired to be secured by Letters Patent is:

1. In a process of treating the surface of metals, the step of subjecting the surface of the metal to be treated to a metal treating agent acting by heterogeneous chemical replacement of said metal by an element, the heterogeneous chemical replacement ingredient of which consists essentially of vapors of a subhalogenide of said element.

2. In a process of treating the surface of metals, the steps of subjecting the surface of the metal to be treated to a metal treating agent acting by heterogeneous chemical replacement of said metal by an element, the heterogeneous chemical replacement ingredient of which consists essentially of vapors of a subhalogenide of said element; and converting the thus formed halogenide of said metal into the original subhalogenide which may be used for the further treatment of metal surfaces.

3. In a process of treating the surface of metals, the steps of subjecting the surface of the metal treated to a metal treating agent acting by heterogeneous chemical replacement of said metal by an element, the heterogeneous chemical replacement ingredient of which consists essentially of vapors of a subhalogenide of said element; removing the thus formed halogenide of said metal from contact with the thus treated metal surface; converting said formed metal subhalogenide into the subhalogenide of an element adapted to react by heterogeneous chemical replacement reaction with a metal; and subjecting the surface of a metal to be treated to vapors of the thus formed subhalogenide.

4. In a process of treating the surface of metals, the steps of subjecting the surface of a metal consisting at least partially of iron to a metal treating agent acting by heterogeneous chemical replacement of said metal by an element, the heterogeneous chemical replacement ingredient of which consists essentially of vapors of a subhalogenide of said element.

5. In a process of treating the surface of metals, the steps of subjecting the surface of a metal consisting at least partially of iron to a metal treating agent acting by heterogeneous chemical replacement of said metal by an element selected from the group consisting of silicon, aluminum, titanium, zinc, antimony, carbon, tin, boron, chromium and copper, the heterogeneous chemical replacement ingredient of which consists essentially of vapors of a subhalogenide of said element.

6. In a process of treating the surface of metals, the step of subjecting the surface of a steel to a metal treating agent acting by heterogeneous chemical replacement of the iron of said steel by an element, the heterogeneous chemical replacement ingredient of which consists essentially of vapors of silicon subchloride.

7. A process according to claim 4 in which said subhalogenide consists of a mixture of aluminum subchloride and silicon subchloride vapors.

8. A process according to claim 4 in which said subhalogenide consists of a mixture of aluminum subbromide and copper subbromide vapors.

9. In a process of treating the surface of metals, the steps of subjecting the surface of the metal to be treated to vapors of a halogenide of an element adapted to react by heterogeneous chemical replacement with said metal; converting the thus formed halogenide of said metal into the subhalogenide of an element adapted to react by heterogeneous chemical replacement with a metal; and subjecting the surface of a metal to be treated to a metal treating agent consisting essentially of vapors of the thus formed subhalogenide.

10. In a process of treating the surface of metals, the step of subjecting the surface of the metal to be treated to a metal treating agent acting by heterogeneous chemical replacement of said metal by an element, the heterogeneous chemical replacement ingredient of which consists essentially of vapors of a subhalogenide of said element in the presence of a metal halogenide adapted to catalyze said reaction.

11. In a process of treating the surface of metals, the step of subjecting the surface of the metal to be treated to a metal treating agent acting by heterogeneous chemical replacement of said metal by an element, the heterogeneous chemical replacement ingredient of which consists essentially of vapors of a subhalogenide of said element in the presence of a metal chloride adapted to catalyze said reaction.

12. In a process of treating the surface of metals, the step of subjecting the surface of the metal to be treated to a metal treating agent acting by heterogeneous chemical replacement of said metal by an element, the heterogeneous chemical replacement ingredient of which consists essentially of vapors of a subhalogenide of said element in the presence of a metal halogenide adapted to catalyze said reaction and being selected from the group consisting of ferric chloride, ferrous chloride, stannic chloride, stannous chloride, aluminum chloride, aluminum bromide, boric fluoride, boric chloride, cupric chloride and magnesium chloride.

13. In a process of treating the surface of metals, the step of subjecting the surface of the metal to be treated to a metal treating agent acting by heterogeneous chemical replacement of said metal by an element, the heterogeneous chemical replacement ingredient of which consists essentially of vapors of a plurality of subhalogenides of said element.

14. In a process of treating the surface of metals, the step of subjecting the surface of a metal consisting at least partially of iron to a metal treating agent acting by heterogeneous chemical replacement of said metal by an element selected from the group consisting of silicon, aluminum, titanium, zinc, antimony, carbon, tin, boron, chromium and copper, the heterogeneous chemical replacement ingredient of which consists essentially of vapors of a subhalogenide of said element in the presence of a metal halogenide adapted to catalyze said reaction.

15. In a process of treating the surface of metals, the step of subjecting the surface of a metal consisting at least partially of iron to a metal treating agent acting by heterogeneous chemical replacement of said metal by an element selected from the group consisting of silicon, aluminum, titanium, zinc, antimony, carbon, tin, boron, chromium and copper, the heterogeneous chemical replacement ingredient of which consists essentially of vapors of a subhalogenide of said element in the presence of a metal halogenide adapted to catalyze said reaction and being selected from the group consisting of ferric chloride, ferrous chloride, stannic chloride, stannous chloride, aluminum chloride, aluminum bromide, boric fluoride, boric chloride, cupric chloride and magnesium chloride.

16. In a process of treating the surface of metals, the steps of oxidizing and subsequently reducing the surface of a metal to be treated so as to chemically activate the same; and subjecting the thus oxidized and reduced surface of said metal to be treated to a metal treating agent acting by heterogeneous chemical replacement of said metal by an element,, the heterogeneous chemical replacement ingredient of which consists essentially of vapors of a subhalogenide of said element.

17. In a process of treating the surface of metals, the steps of oxidizing and subsequently reducing the surface of a metal to be treated and consisting at least partially of iron so as to chemically activate the same; and subjecting the thus oxidized and reduced surface of said metal to be treated to a metal treating agent acting by heterogeneous chemical replacement of said metal by an element, the heterogeneous chemical replacement ingredient of which consists essentially of vapors of a subhalogenide of said element.

18. In a process of treating the surface of metals, the steps of oxidizing and subsequently reducing the surface of a metal to be treated and consisting at least partially of iron so as to chemically activate the same; and subjecting the thus oxidized and reduced surface of said metal to be treated to a metal treating agent acting by heterogeneous chemical replacement of said metal by an element selected from the group consisting of silicon, aluminum, titanium, zinc, antimony, carbon, tin, boron, chromium and copper, the heterogeneous chemical replacement ingredient of which consists essentially of vapors of a subhalogenide of said element.

References Cited in the file of this patent

UNITED STATES PATENTS

1,497,417	Weber	June 10, 1924
2,219,004	Daeves et al.	Oct. 22, 1940
2,344,138	Drummond	Mar. 14, 1944
2,501,051	Henderson et al.	Mar. 21, 1950
2,604,395	Gonser et al.	July 22, 1952
2,622,043	Roush	Dec. 16, 1952
2,656,284	Toulmin	Oct. 20, 1953
2,731,361	Mack et al.	Jan. 17, 1956