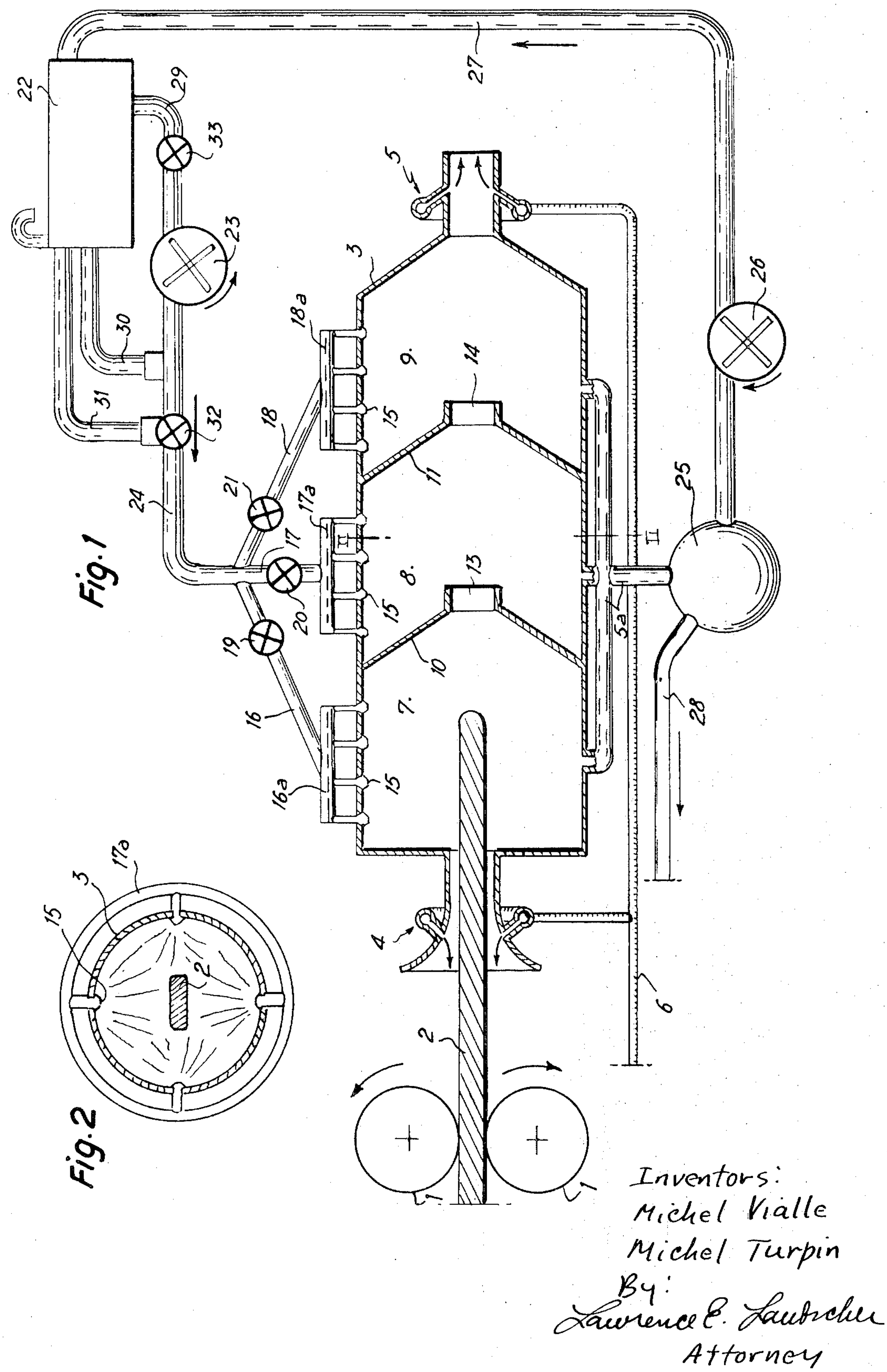
July 30, 1974 M. VIALLE ET AL 3,826,681

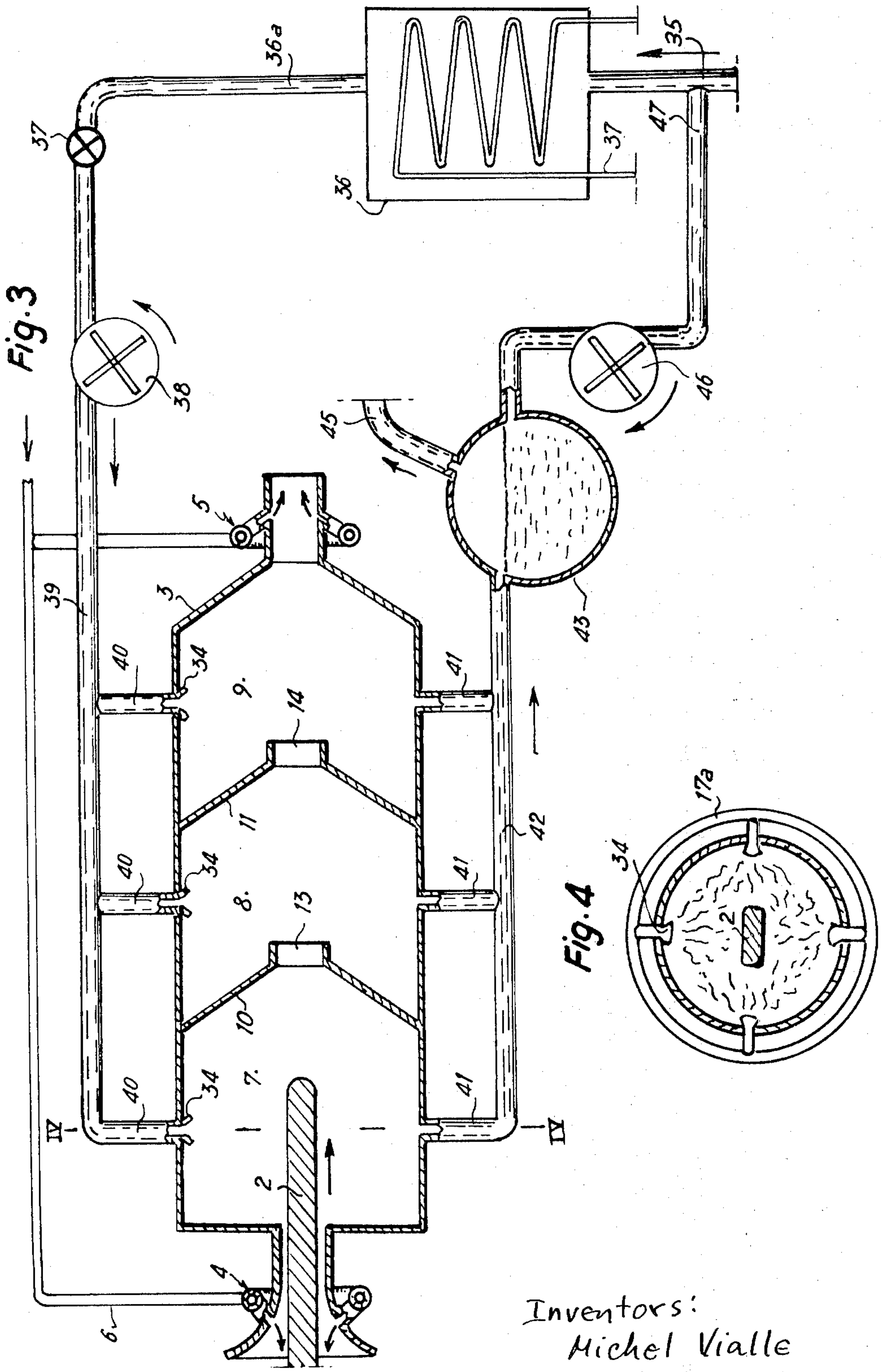
METHOD FOR PROTECTING A HOT ROLLED FERROUS PRODUCT

Filed Feb. 4, 1971 3 Sheets-Sheet 1



METHOD FOR PROTECTING A HOT ROLLED FERROUS PRODUCT

Filed Feb. 4, 1971 3 Sheets-Sheet 2

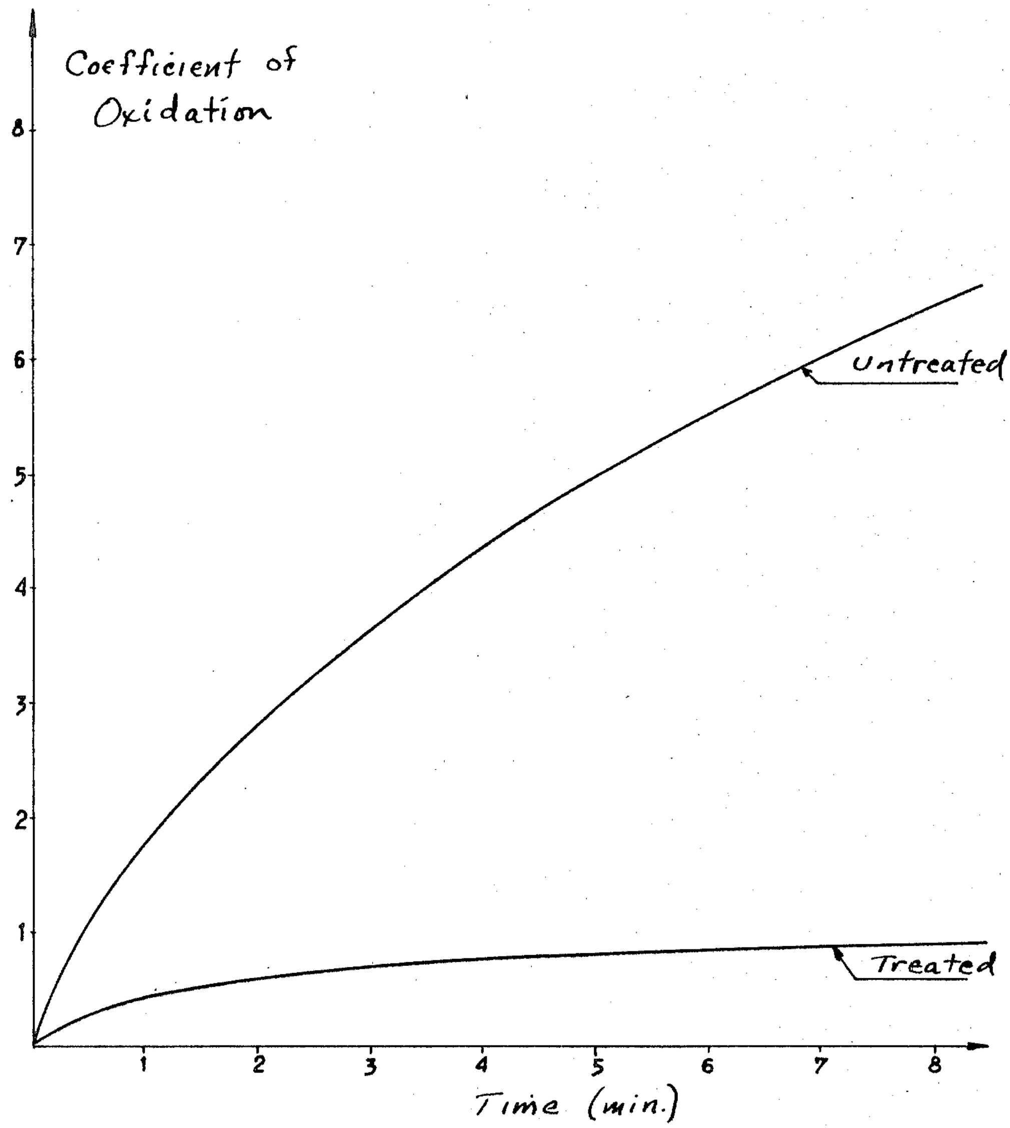


Inventors:
Michel Vialle
Michel Turpin
By:
Lawrence E. Laubscher
Attorney

METHOD FOR PROTECTING A HOT ROLLED FERROUS PRODUCT

Filed Feb. 4, 1971 3 Sheets-Sheet 3

Fig. 5



Inventors:
Michel Vialle
Michel Turpin
By:
Lawrence E. Laubscher
Attorney

United States Patent Office

3,826,681

Patented July 30, 1974

1

3,826,681

METHOD FOR PROTECTING A HOT ROLLED FERROUS PRODUCT

Michel Vialle, Thionville, and Michel Turpin, Bourg-la-Reine, France, assignors to Societe Wendell-Sidelor, Societe Anonyme, Hayange, France

Filed Feb. 4, 1971, Ser. No. 112,594
Claims priority, application France, Feb. 9, 1970, 7004451
Int. Cl. C23c *11/06*
U.S. Cl. 117—135.1 10 Claims

ABSTRACT OF THE DISCLOSURE

A method for de-scaling a hot-rolled ferrous product, together with the de-scaled protected ferrous product produced thereby, characterized by the formation on the ferrous product as it leaves the rolling mill of a protective iron-silicon surface layer. More particularly, the ferrous product, as it leaves the rolling mill at a temperature of from between 800° C. to 1200° C., is sprayed with a de-scaling material comprising a chlorinated compound of silicon, and preferably a chlorinated derivative of silane.

The present invention relates to a method for de-scaling and protecting against subsequent oxidation or scaling a hot-rolled ferrous product, such as thick, medium or thin sheets, bars, structural shapes, wire and the like.

It is known in the prior art to pickle a metal article by dipping it in an acid bath (for instance, a diluted sulphuric acid bath). In this process the layer of scale is actually removed, but at the same time the iron is slightly attacked, and consequently there is an additional loss of metal. The process of "de-scaling" is also known, which is mainly used when drawing wire, whereby the wire is bent in order to crack and loosen the scale and thus get rid of it.

Both of the aforementioned processes present certain drawbacks. In the case of dipping, the product is put into a low temperature bath, preferably less than 100° C., which means that in the case of hot-rolled products there is a waiting period before the scraping can begin. Such a process is time-consuming, since products such as commercial iron when it finally comes out of a rolling mill housing, have a temperature of about 1000° C. Furthermore the dipped products oxidize again if they are not subjected immediately to another treatment. The same is true for the mechanical de-scaling which still leaves the possibility of reoxidation.

As is well kown in the art, the two processes mentioned above are generally preceded at the time of rolling of the semi-finished products and even in the case for instance of merchant bars by a water spraying or steaming operation which takes place during the rolling process itself. More particularly, water or steam is sprayed onto the products that are being rolled, whereby a first coat of scale is at least partially removed. But if the products are not immediately protected while hot, a re-oxidation of the product takes place during their cooling.

This water spraying process has been proposed in order to supply a protective liquid which vaporizes when it enters into contact with the hot surface of the rolled product and deposits on it a protective film. It has also been proposed to separate the water spraying process from the spraying of the protective liquid. In any event, the products which were previously proposed do not permit the protection of the article in only one step. The aim of the present invention is to avoid all these inconveniences and to provide a protective material that is operable in one step to practically eliminate at a high temperature all the scale which covers the metallurgical products during their hot rolling process, and to assure at the same time their protection against subsequent re-oxidation.

2

Accordingly, the primary object of the present invention is to provide a material for de-oxidizing and protecting ferrous products against oxidation during the hot rolling process, characterized in that the treating material is a chlorinated compound of silicon. This protective material, in accordance with the present invention, comprises either a chlorinated compound of silicon which only contains silicon and chlorine, a chlorinated derivative of silane (specifically, methyltrichlorosilane), a chlorinated derivative of silane which only contains the elements silicon, chlorine and hydrogen, a chlorinated derivative of silane which only contains the elements silicon, chlorine, hydrogen and carbon, a chlorinated derivative of silane of the type $RSICl_3$, R being an organic radical, a chlorinated derivative of silane of the type R_2SiCl_2, R_2 being an organic radical, or a chlorinated derivative of silane of the type R_3SiCl, wherein R_3 is an organic radical. In accordance with another feature of the invention, a chemically active body is added to the de-scaling materials, or a body which is substantially chemically inert relative to the ferrous products at a temperature of at least 800° C. is added to said de-scaling material.

A further object of the present invention is to provide a process for applying the above-mentioned material, which process is characterized by passing the hot rolled ferrous product as it comes out of the rolling mill through a closed housing within which the de-scaling and protective material is sprayed onto the rolled product at a temperature ranging between 800° and 1200° C.

According to a more specific object of the invention, the de-scaling material is sprayed in atomized form. On the other hand, the de-scaling material may be emulsified in a carrier gas or evaporated to the vapor stage by a heater or boiler for circulation through the housing. Finally, the de-scaling material may be injected in a liquid or gaseous condition into a reducing flame which licks the hot rolled product.

A further object of the invention is to provide apparatus for performing the above mentioned process, including a housing through which the ferrous product passes, inert gas seal means for sealing the entrance and exit openings of the housing, and means for spraying the de-scaling material onto the rolled products. According to one embodiment, the de-scaling material is sprayed in atomized form onto the hot rolled product, while in another embodiment, boiler means are provided for vaporizing the de-scaling material prior to spraying. The housing includes a plurality of chamber sections which are separated by partitions that contain coaxially arranged openings which permit the hot-rolled product to pass therethrough, the spray means being arranged in such a way as to spray the product at different angles, whereby means are provided for regulating the discharge in each chamber. The means for spraying the de-scaling material onto the rolled products include openings connected with heater means which vaporize the de-scaling material or which emulsify it in a gas carrier. The housing includes several chambers separated by partitions that contain coaxial openings through which the rolled ferrous product is transported, and means are provided for regulating the intake of vapors in each chamber.

Finally, the invention also relates to the resultant ferrous product that is produced by the aforementioned process and apparatus, which product is protected against re-oxidation by a protective surface layer comprising a simple or complex iron-silicon compound.

For the better understanding of the invention, several examples and applications are given hereafter, which are in no way restrictive of the invention, reference being made to the accompanying drawing, in which:

FIG. 1 is a schematic view in a vertical section of a first embodiment of the apparatus of the present invention, wherein the de-scaling material is applied in atomized form with the aid of a carrier;

FIG. 2 is a sectional view taken along line II—II of FIG. 1;

FIG. 3 is a schematic vertical section of a second embodiment which sprays the de-scaling material in the form of a vapor;

FIG. 4 is a sectional view taken along line IV—IV of FIG. 2; and

FIG. 5 shows two representative curves of the oxidation coefficient of a wire treated by the process according to the invention and of a standard comparison wire at 1000° C. temperature.

In accordance with the present invention, the most adequate material for de-scaling and simultaneously protecting a hot rolled ferrous product against oxidation is a chlorinated compound of silane which may contain an organic radical.

One example which gives a particularly satisfactory result has been found to be methyltrichlorosilane

$$(CH_3SiCl_3)$$

which material is a liquid body under atmospheric pressure and ambient temperature. During the tests, it was established that methyltrichlorosilane, when sprayed on a ferrous product between 800 and 1200° C. (which is the optimal range of temperatures), ignites spontaneously when in contact with the air. Consequently, the advisable application of this material is for it to be sprayed in a sealed housing through which the product to be protected is transported, in order to avoid contact between the methyltrichlorosilane vapor, at a high temperature, with the oxygen of the air.

It has also been noted that it may be desirable to add to the methyltrichlorosilane or similar substance a material (such as lime or silica) that is inert or substantially chemically inert to the ferrous product at the rolling temperature. The inert substance can in a certain way play the role of a load for facilitating the distribution of the de-scaling product.

Other examples of chlorosilane compounds which also give favorable results are:

Ethyltrichlorosilane	$C_2H_5SiCl_3$.
Dimethyldichlorosilane	$(CH_3)_2SiCl_2$.
Triphenylchlorosilane	$(C_6H_5)_3SiCl$.

The reaction between the silane compounds and the ferrous product takes place at a high temperature at approximately 1000° C. (as it is mentioned above in the case of methyltrichlorosilane). Consequently, according to the temperature of the product, it may be useful in order to obtain the desired reaction, either to reheat the surface of the product before treatment, or to reheat the vapors of the reacting material, or to use the atomization of this material or emulsion in a carrying gas or a preliminary boiling, or an injection of the liquid or gaseous material into a reducing flame.

Referring now to the drawing, FIGS. 1 and 2 illustrate an apparatus for spraying atomized particles of the treating material. Two rolls **1—1** of the rolling mill have been shown schematically for supplying the hot rolled ferrous product **2**. In the interest of simplification, the rolled product **2** has been shown as entering into the device immediately after the last roll pair of the hot rolling mill. This of course is not always necessary. Actually, according to the kind of rolling mill, the installation may be before the first stand, after the last stand, or even between the former and the latter. A reheating of the product when using methyltrichlorosilane is not always necessary because after last pass the rolled products are more or less at the desired temperature.

The device comprises a housing **3** through which the rolled product is transported. At the entrance and exit openings **4** and **5**, respectively, of the housing, injection means are provided for supplying an inert gas (as, for example, nitrogen, argon or another appropriate gas) via the supply pipe **6**. Housing **3** includes three chambers, **7**, **8** and **9** defined by partitions **10**, **11**, which partitions contain co-axial openings **13** and **14** which receive and guide the bar **2**.

While a bar with a rectangular section has been illustrated in the drawing, it is apparent that the device can also be used in connection with products having square, circular and other profile cross sectional configurations.

Each chamber has a plurality of pulverizing nozzles **15** which are supplied with fluid through pipes **16**, **17**, **18** via distribution manifolds **16*a***, **17*a***, **18*a***. The pipes are provided with valves **19**, **20**, **21** which afford independent regulation of the flow of the liquid into each chamber. Furthermore the injection nozzles **15** are directed differently in each chamber in order to achieve a complete application of the de-scaling material.

The atomization circuit, which is conventional, comprises also a container **22** which contains the material which is being used, for instance methyltrichlorosilane. The liquid is fed into the atomizer means by means of a pump **23** which discharges onto a pipe **24**. On the other hand, the liquid coming from the operation is re-cycled through a separation reservoir **25** and a pump **26**, and forced back through a pipe **27** into the vat **22**. The reservoir **25** which receives the liquid through a collection manifold **5*a*** is provided with an overflow **28**.

Adjacent the container **22** pipes **29**, **30** and **31** and valve means **32** and **33** are provided for isolating the container from the atomization circuit and for regulating the flow of material.

FIGS. 3 and 4 show an installation which applies the treating material through vaporization. In these figures, parts shown with the primed reference numbers correspond with similar elements in FIGS. 1 and 2. Here each chamber is provided with openings **34** through which the vapors of the de-scaling product arrive. The vaporizing circuit is also conventional. The de-scaling liquid arrives through a pipe **35** into a boiler **36** inside of which a heating coil **37** has been installed. The vapor comes out through pipe **36*a*** and is supplied to the openings **34** via the regulating valve **36*b***, the accleration pump **38**, conduit **39** and distributor pipes **40**.

The excess product flows out at the lower part of the enclosure through pipes **41** and return pipe **42** into a separation and condensation sphere **43** provided with an exhaust conduit **45**. A pump **46** returns the liquid product to the boiler **36** via return pipe **47**.

Of course the gaseous reagent which circulates between the evaporating boiler **36** and the housing **3** is maintained at an adequate temperature in order to avoid its condensation by means of considerable insulation or a heating flue.

The products obtained through this process and by means of the devices which have been described are of a very particular nature and have exceptional qualities.

Analyses performed have shown that the protective surface layer obtained in accordance with the present invention has an iron-silicon compound base, and that the layer is extremely thin. Furthermore its aspect is particularly satisfactory and for instance samples of wire treated in this manner have a brilliant aspect after having been dipped in nitrogen or argon in order to bring them back to the ambient temperature.

On the other hand the resistance to reoxidation when in contact with air, even at a temperature of 1000° C., is much higher than that of the common products.

Referring to FIG. 5, the two curves illustrate, respectively, the oxidation coefficient of a wire treated in accordance with the present invention, and the oxidation coefficient of a reference sample wire. The abscissa and ordinates of this figure illustrate, respectively, the time in minutes and the oxidation coefficient (i.e., the weight increase in mg. per $cm.^2$ due to the oxidation of the metal). It is apparent that the resistance to oxidation of the treated wire is infinitely superior to that of the non-treated wire.

While in accordance with the provisions of the patent statutes the preferred form and embodiments have been illustrated and described, it will be apparent that various changes may be made without deviating from the inventive concepts disclosed herein.

What is claimed is:

1. The method of simultaneously descaling and protecting from oxidation ferrous products immediately following the hot rolling thereof, which comprises the steps of

passing the rolled product, after it leaves the rolling stand, through a chamber having inlet and outlet openings provided with barriers of an inert gas; and

projecting onto the rolled product, while within the chamber and at a temperature of between 800° C. and 1200° C., a chlorine-containing compound of silicon.

2. The method as defined in claim **1**, wherein said chlorine-containing compound of silicon consists solely of silicon and chlorine.

3. The method as defined in claim **1**, wherein said chlorine-containing compound of silicon comprises a chlorinated derivative of silane.

4. The method as defined in claim **3**, wherein said chlorine-containing derivative of silane consists of silicon, chlorine and hydrogen.

5. The method as defined in claim **3**, wherein said chlorine-containing derivative of silane consists of silicon, chlorine, hydrogen and carbon.

6. The method as defined in claim **3**, wherein the chlorine-containing derivative of silane is of the type $RSiCl_3$, R being an organic radical.

7. The method as defined in claim **3**, wherein the chlorine-containing derivative of silane is of the type R_2SiCl_2, R being an organic radical.

8. The method as defined in claim **3**, wherein the chlorine-containing derivative of silane is of the type R_3SiCl, R being an organic radical.

9. The method as defined in claim **3**, wherein the chlorine-containing derivative of silane is methyltrichlorosilane.

10. The method as defined in claim **1**, wherein said ferrous product is treated with said chlorine-containing compound of silicon in the absence of oxygen.

References Cited

UNITED STATES PATENTS

2,442,485	6/1948	Cook	117—53
3,438,802	4/1969	Kanter	117—106 A
2,458,655	1/1949	Sowa	117—106 A
2,501,051	3/1950	Henderson et al.	117—106 A

WILLIAM D. MARTIN, Primary Examiner

J. A. BELL, Assistant Examiner

U.S. Cl. X.R.

117—106 A, 118