

UNITED STATES PATENT OFFICE

2,644,775

METHOD OF BRIGHT ANNEALING AND
CLEANING

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No Drawing. Application July 1, 1950,
Serial No. 171,757

10 Claims. (Cl. 148—14)

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This invention relates to methods for treating metallic articles and more particularly to processes for annealing metals whereby substantially oxide-free bright smooth metallic surfaces are produced.

It is an object of this invention to provide a process which produces annealed metallic articles having bright smooth surfaces which are free of objectionable surface oxides, thus obviating the need for subsequent pickling treatments for the removal of such oxides which are formed during the annealing process. Other objects will be apparent to those skilled in the art and still others will be evident from the following description of this invention.

According to my invention metallic articles are stress and strained relieved or annealed without the formation of an objectionable surface oxide thereon, but rather in a manner so that the treated metal possesses a bright clean smooth unpitted surface by the method which comprises: subjecting ferrous metal articles, in a confined heat treating zone, to the action of the fumes produced by a fused composition of alkali metal hydroxide and alkali metal fluoride, maintained at an elevated temperature sufficient to cause fuming, until an adhering film is deposited upon the surface of the metal, whereupon the metal so treated is then subjected to annealing conditions in a second heat treating zone, preferably in heat communication with the first zone, maintained at a temperature at least above the temperature of the first zone, said temperature being sufficiently high for annealing purposes, thereafter cooling the metal, and thence quenching or washing the metal so treated in water to remove the protective film from the metal surface thereby producing an annealed metal having a bright smooth unpitted surface.

By proceeding in accordance with my invention, the surface of the metallic article to be stress relieved is uniformly preheated and coated with the fumes of my salt composition, which have a particular affinity for the metallic surfaces to be treated, especially for the surfaces of low or high carbon steels, including stainless steels, which have been previously hot or cold worked under ordinary oxidizing conditions. The salt coating produced on the surface of the metal in the first step of this process is bound to the metal with sufficient tenacity to prevent its removal during the subsequent annealing and cooling steps, where it acts as a protective coating preventing undesirable oxidation of the metallic surface, but said coating is easily removable dur-

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ing the quenching step because of its ready solubility in water. In addition, my invention is easily adaptable for use in commercial installations having customary annealing furnaces because the fumes produced by heating my compositions containing alkali metal hydroxide and between about five and forty per cent by weight of alkali metal fluoride are not corrosive to the furnace walls which are made of ordinary refractory material. This is somewhat surprising in view of the known corrosive action of caustic soda and its fumes at temperatures of about 1300° F. on the refractory materials used in furnace construction. It is also somewhat unexpected to find that by operating in accordance with my invention the surface of the treated work is not pitted, as would be the case if the fumes of caustic soda alone were used to produce the protective coating which prevents oxidation of the surface during annealing.

In order that this invention may be more readily understood it will be described in connection with a preferred embodiment thereof, however, it is to be understood that this invention is not to be construed as limited thereto, as will be more evident from the various modifications discussed hereinafter.

A continuous sheet of cold worked 18-8 type stainless steel having a bright clean metallic surface free of oxides, is introduced through an asbestos curtain into a bi-zoned annealing furnace having an ordinary refractory lining. The furnace is approximately 50 feet long and about 12 feet wide, and is preferably sectioned lengthwise by baffles into a first or coating zone of approximately one-fifth the entire length. The first zone of the furnace is maintained at a temperature of about 1400° F. and contains the fumes produced by a fused mixture of sodium hydroxide and sodium fluoride containing about 20 per cent by weight of the latter. The fused salt mixture is contained in a pan about 6 feet long, 12 inches wide, and 10 inches deep, and is housed near the bottom of the first zone of the furnace. The furnace is preferably equipped with means for circulating the fumes within the first zone of the furnace, for example, by locating the suction pipe of a blower at the bottom of the furnace near the furnace inlet with the discharge pipe being located at the top of the furnace and positioned more removed from the furnace inlet than the suction pipe. The second or stress relieving zone is an extension or continuation of the first zone of the furnace except that it is divided therefrom by baffles which are designed

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to favor the retention of the salt fumes in the first zone. In addition, the second zone is maintained at annealing temperatures which are at least about 100 Fahrenheit degrees above the coating and preheating temperatures maintained in the first zone, thus further favoring the retention of the salt fumes in the first zone. The sheet of steel is continuously passed into the first zone of the furnace through the asbestos curtain, at a rate which allows a contact time between the metal and the fumes within the first zone of about one minute, or for a time sufficient to allow a yellow-white coating in more or less uniform distribution to be deposited on the surface of the metal. Upon obtaining said deposit on the surface of the metal and having obtained a substantially uniform heating of the metal to the temperature maintained in the coating zone, the sheet is then continuously passed, at substantially the same rate it was being moved through the first zone, into the second annealing zone which is maintained at a temperature up to 1950° F. The metal is retained in the annealing zone for a longer period of time because of the greater length to be traversed and is retained therein until the metal is annealed. Thereafter, the sheet is continuously moved out of the furnace into the atmosphere whereupon it is cooled to a temperature of about 200° F., and after which it is quenched in water. The yellow-white deposit which acted as a protective coating preventing oxidation of the metal surface during annealing is readily dissolved in water, thus leaving a bright oxide-free smooth unpitted surface, comparable to that of the untreated metal, on the metallic article which is annealed or stress relieved.

In a manner similar to the foregoing procedure low carbon mild hot rolled strip steel having a dark brown or black oxide coating was treated as above outlined except that the composition of the salt comprised 90 per cent caustic soda and 10 per cent sodium fluoride, the temperature in the coating zone was maintained at about 1250° F., and the temperature in the annealing zone was maintained up to a temperature of 1400° F. The contact time of the metal with the fumes of the salt composition was approximately one minute; and, the contact time in the annealing zone of the furnace was about four minutes. The surface of the metal removed from the furnace was coated with a protective film which prevented oxidation of the surface during the annealing operation and also when the metal was air cooled to about 300° F. prior to quenching in water. The surface of the finished annealed metal after quenching was brighter and cleaner than the surface of the metal originally introduced into the furnace. In addition, after continuous operation in said furnace no apparent corrosion of the furnace walls was evident.

The metals which may be treated in accordance with my invention are the ferrous metals. Besides iron, the other metals of the ferrous group including nickel, cobalt and their alloys with each other and with chromium, manganese, molybdenum, tungsten, vanadium and copper are successfully bright-annealed by my process. The shape of the metal to be treated is not particularly important and in addition to sheets and strips of metal, such forms as bars, tubing, plates, fabricated articles, etc., may be successfully processed either continuously, batch-wise or intermittently in accordance with my invention. Metal articles which have been cold or hot worked may

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be bright annealed by my methods, and in the case of hot rolled steel having a surface oxide thereon produced during working, my process can effect a substantial removal of such oxide leaving a bright smooth unpitted metallic surface which is better than that of the metal originally introduced into the furnace.

The exact conditions to be maintained for obtaining optimum results are dependent on various factors such as the kind of metal being treated, the nature of the previous treatments the metal has been subjected to, the size and shape of the metal, etc. In general, I have found that satisfactory results may be obtained by subjecting ferrous metals to the fumes produced by a composition of sodium hydroxide and five to forty per cent by weight of sodium fluoride maintained at a temperature above about 1200° F. until a substantially uniform coating is deposited on the metal surface, before subjecting the metal to annealing temperatures maintained in the second zone. It is also preferable to air cool the metal removed from the second annealing zone to a temperature between about 150° F. to 350° F. prior to quenching in the water.

The time for coating is a variable which is dependent on various factors, principally the concentration of the fumes in the coating zone, the temperature maintained in the coating zone, and the kind, size and shape of the metal to be treated. I have found that good results may be obtained by allowing a time of contact between the metal and the fumes of between five seconds and five minutes in the coating zone.

The temperature to be maintained in the annealing or stress relieving zone is preferably higher than the temperature maintained in the coating zone. It is advantageous to utilize the first zone of the furnace for the combined purposes of preheating the metal to a temperature approaching the annealing temperature and also for providing the metal with a protective coating prior to the stress relieving or annealing step in this process. Also, it is advantageous to combine the air cooling step in my invention with any modification in cooling from the annealing temperature to the quenching temperature for the purpose of securing specific advantages from such modifications.

In the foregoing examples, treatment of low carbon steel and stainless steel have been illustrated. In general, the various modifications of steel commonly classified as falling between these two types, may be successfully treated under conditions between those defined in the examples. It should be noted that various other alkali metal hydroxides and various other alkali metal fluorides may be successfully used in accordance with my invention, but that mixtures of the hydroxide and fluoride of sodium are preferred because of their satisfactory performance, commercial availability, and economy. The proportion of fluoride to be combined with the caustic may be varied between about five and forty per cent by weight. More than forty per cent has been found ineffective for general purpose usage and too inactive, and less than five per cent has been found to be undesirable because of excessive corrosion on the furnace walls and corrosion and pitting of the base metal. Best results are obtained by using a caustic composition containing between 10 and 30 per cent sodium fluoride.

Although I have described my invention in connection with certain specific embodiments there-

of, I do not intend to be limited thereto except as defined in the appended claims.

I claim:

1. In a method for producing annealed bright surfaced metallic articles, the step comprising: 5
subjecting the article in a confined zone to the action of the fumes produced by maintaining a composition of alkali metal hydroxide and alkali metal fluoride at a temperature sufficient to cause fuming until a protective coating of said composition is deposited on the metallic surface and removing said coating by contacting with water. 10

2. In a method for annealing a metallic article whereby a bright unpitted metallic surface is produced, the step comprising: 15
subjecting the article in a confined heated zone to the action of the vapors of a mixture of sodium hydroxide and sodium fluoride until a protective coating of said composition is deposited on the metallic surface and removing said coating by contacting with water. 20

3. A process for heat treating metallic articles comprising subjecting the metal to the action of the fumes of a mixture of sodium hydroxide and sodium fluoride, until a protective coating of said composition is deposited on the metallic surface, annealing the metal, and subsequently removing the protective coating by quenching the article in an aqueous medium. 25

4. A process for annealing metallic articles to produce a bright clean unpitted surface thereon which comprise, contacting the surface of the metal with vapors of a caustic alkali composition containing between about five and forty per cent alkali metal fluoride, at a temperature above about 1250° F., for a period of at least five seconds, annealing the metallic article at a temperature above about 1350° F., cooling the article to between about 150° and 350° F. and quenching the article in an aqueous medium. 30

5. In a method for preventing oxide formation on the surface of metal articles during annealing, the improvement comprising coating the surface of such articles with a protective film of a composition comprising sodium hydroxide and sodium fluoride by exposing the articles in a confined zone to the vapors produced by maintaining said composition at a temperature sufficient to cause fuming prior to the annealing operation. 35

6. A continuous process for producing an annealed oxide-free bright surfaced metallic article comprising contacting the article in a confined preheating zone maintained at a temperature above 1250° F. with the vapors of a sodium hydroxide-sodium fluoride composition, until an adhering film is deposited on the metallic surface, heating the metal to annealing temperatures in a second heat treating zone, until the article is stress and strained relieved, subjecting the metallic article to atmospheric cooling and quenching 40
the article in water. 45

7. In a process for removing surface oxide from metallic articles, which has been formed thereon by hot working, whereby a bright clean unpitted metallic surface is produced, the method which comprises, contacting the metallic surface with sodium hydroxide-sodium fluoride vapors in a confined heated zone until a protective coating is deposited on the surface of the metal and removing said coating by dissolving it in water. 5

8. A bright annealing process for ferrous metallic articles comprising preheating the article in a confined zone containing the vapors produced from a mixture of alkali metal hydroxide and alkali metal fluoride maintained at a temperature sufficient to cause fuming, annealing said treated article in an annealing zone at a temperature of at least about 100 Fahrenheit degrees above the temperature of the preheating zone, and quenching the metallic article. 10

9. A bright annealing process for ferrous metallic articles comprising preheating the article in a confined zone containing the vapors produced from a mixture of alkali metal hydroxide and alkali metal fluoride at a temperature above about 1250 degrees Fahrenheit, to deposit a protective coating on the surface of the metallic article, annealing the article in an annealing zone at a temperature of at least about 100 Fahrenheit degrees above the temperature of the preheating zone, air cooling the metallic article and removing the protective coating by dissolving it in water. 15

10. A bright annealing process for ferrous metallic articles comprising preheating the article and applying a protective coating on the surface thereof by exposing the article in a confined zone to the vapors produced from a mixture of sodium hydroxide and sodium fluoride maintained at a temperature above 1250 degrees Fahrenheit, annealing the coated article in an annealing zone at a temperature of at least about 100 Fahrenheit degrees above the temperature of the preheating zone, cooling the article and quenching the metallic article to remove the protective coating. 20

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