United States Patent Office 3,725,141
Patented Apr. 3, 1973

3,725,141

ANNEALING STEEL PRODUCTS

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No Drawing. Filed Nov. 10, 1971, Ser. No. 197,317
Int. Cl. C21d 1/76
U.S. Cl. 148—16 15 Claims

ABSTRACT OF THE DISCLOSURE

Carbon deposition is avoided in a process for annealing steel products with residual lubricants thereon, by introducing a lower alkyl alcohol into the annealing chamber during the early stages of the heating processes. Catalysts such as HCl also may be used.

The present invention relates to a process for heat treating of steel products, more particularly to a process for heat treating steel products having residual lubricants thereon which process avoids the formation of carbon deposits on surfaces of the steel products.

During the fabrication of many types of steel products, such as steel coil, lubricants such as oil, grease, solutions of oil or grease, or emulsions of water and oil are used to lubricate the steel during the rolling, drawing, or forming operations. For instance, lubricants used in cold rolling steel coil are generally aqueous emulsions of fatty acids, or fatty acids soaps and mineral oil. As a result of the use of the lubricants, the steel coils or other steel products arrive at the annealing furnace with a film of lubricant deposited thereon. While it is possible to wash the steel products with various solutions such as an alkaline wash which will remove most of the lubricant, the wash step is expensive, time consuming and not always as successful in removing the lubricant entirely.

The prior art has recognized the connection between lubricants and carbon spots or snakey-edge formation on annealed steel coil. It is generally believed that when steel articles coated with such oil or grease are subjected to an annealing treatment in a furnace, that the lubricants or grease decomposes by a mechanism which is not fully understood, but the result is that carbon is deposited on the articles being annealed.

Snakey-edge or carbon edge has been recognized in the prior art as a particularly troublesome problem encountered by steel mills which produce cold rolled strip. According to the prior art, snakey-edge is evidenced in cold rolled steel coils by a wavy band, varying in degrees of darkness, found near the edge of strip or sheets after annealing. The condition is characterized by a black deposit which is sharp at the outer limit and gradually defusing into the steel background as it penetrates towards the center of the sheet or strip. The extreme edge of the sheet so effected is always very clean and bright. The sharp transition from bright steel to black may occur in a distance up to approximately 1 inch from the coil edge, while the width of the band itself can vary from a pencil line thickness up to two inches or more. The principal reason that this condition is objectionable is because it effectively produces an unwettable surface, i.e., it is lyophobic. This leads to difficulties where coatings such as zinc, tin, or paint are to be applied to the surface, and also interferes with lithograph work.

The prior art has not been consistent in describing the causes of carbon snakes. It has been postulated that

snakey-edge arises during the annealing operation from the catalytic breakdown of carbon containing gases, and that the primary catalysts for this breakdown are the finely divided scale of iron particles arising from service breakdown during rolling. Other prior art, such as U.S. Pat. Nos. 2,504,808, 3,167,459 and 3,531,333 have attributed the snakey-edge to the breakdown or cracking of the lubricants used for rolling which are present on the surface of the steel products being annealed. Other prior art ascribes the problem to a combination of both theories.

Included in the prior art attempts to reduce the formation of carbon snakes were adjustment of the quantity, type, pH, and concentration of the oils in the rolling oil emulsion lubricant. While some improvement was noted by carefully adjusting these materials, the problem was not eliminated.

The prior art has also suggested that the problem of carbon deposition can be obviated by adjusting the gas used in the annealing furnace. The prior art has also reported that during the annealing process, variations as to the heating rate, the purging time, the furnace design, and alterations to the compositions of the gases used showed no significant effect on the incidents of snakey-edge. Although the solutions to the problem suggested by the prior art appear to be occasionally successful, they have not been uniformly successful in eliminating the deposition of carbon on the steel products during the heating operation.

According to the prior art it is known that the lubricants used on steel products are susceptible to cracking during the annealing process causing the formation of carbon as a residue which is deposited on the steel. While it is possible under some circumstances to vaporize or volatilize the lubricants without the deposition of carbon on the steel products, problems are encountered in that the vaporization temperatures are quite high and are very nearly the same as the cracking temperatures. Further, during conventional annealing processes, the temperature is increased at a rate which is too rapid to permit complete vaporization of the lubricants, and the cracking temperature is thereby attained before the lubricants are vaporized. The cracking of the lubricants results in deposition of the carbon on the steel products.

The present invention is based on the observation that carbon formation is obviated by the addition of methanol vapors to the annealing furnace during the initial heating of steel products with lubricants thereon. It is postulated that by heating the steel with the lubricant residue to an elevated temperature, below the decomposition temperature of the lubricants, and such lubricants are reacted with alcohol vapors to form relatively volatile esters which may be vaporized from the surface of the steel products without any traces of carbon deposition. Although it is difficult to determine precisely what reactions are taking place during this process, it is believed that the lower alkyl alcohols such as methyl alcohol will react with the fatty acid components of the lubricants to form esters, and react with the fatty acids soaps, in a transesterification reaction, to form esters, which are thereby vaporized without decomposition. It is known that the vaporization temperature of organic esters is generally considerably lower than the vaporization temperature of the corresponding acids and of the corresponding soap. Thus, it is believed that the process of the persent invention converts the soaps and the fatty acids to the respective esters

which volatilize at a lower temperature, thus, enabling the vaporization process to be completed before the temperature reaches the decomposition or cracking temperature of the fatty acids, the fatty acids soap, or the ester per se. It is postulated that the ester form of the lubricants are vaporized before any significant amount of cracking takes place, and as a result the formation of carbon on the steel surfaces is largely obviated.

In carrying out the process of the present invention, good results have been obtained through the use of methanol, but the present invention contemplates using lower alkyl alcohols having up to about 5 carbon atoms. However, methanol is preferred because of its low cost and because it forms the lowest molecular weight esters.

It has been further discovered that the reaction between the lower alkyl alcohol and the lubricant components may be accelerated by the use of catalysts. While the preferred catalysts for use with methanol is hydrogen chloride gas, boron trifluoride has also given good results. The present invention also contemplates using other catalysts such as silica, zinc chloride, tin chloride, aluminum chloride, iron chloride, dihydroxy fluoroboric acid, soap (such as the soaps which make up a portion of the lubricant), aluminum silicate, hydrobromic acid, hydrofluoric acid, aromatic sulfonic acid, lead, antimony, bismuth, titanium, manganese, alkali and alkaline earth compounds, alloys of tin, manganesium oxide, phosphoric acid, sulfuric acid and mixtures thereof, as well as others. It will be obvious to those skilled in the art that many of the aforementioned catalysts such as manganese, soaps, iron and iron chloride may be present in or on the steel product to be heat treated. It is obvious that little if any additional catalyst is required to carry out the reaction. However, it is contemplated that the addition of specific catalsyts will sometimes accelerate the reaction to a desirable extent. Although it is generally preferred to use catalysts which can be volatilized with the alcohol vapors, catalytic materials which are components of the steel products or the lubricants would not seem to require volatilization. Since the exact mechanism and situs of the reaction is not known, it is possible that a nonvolatile catalyst placed in the base of the annealing furnace, for instance would be effective.

The amount of alcohol required to carry out the process of the present invention must be adequate to react with substantially all of the lubricants present on the steel being annealed. It is believed that the presence of excess quantities of alcohol are not harmful, but are wasteful from an economic point of view. The examples herein illustrate the use of between 500 ml. and 1500 ml. of methanol in a box anneal of about 280 cubic feet to give a gross methanol concentration of from about 1.8 to about 5.4 ml. per cubic foot. However, since the annealing furnace usually contains from about 30 to about 45 tons of steel which weighs about 450 pounds per cubic foot, and occupies from about 130 to about 200 cubic feet, the net free volume in the furnace runs from about 80 to about 150 cubic feet, to give a net methanol concentration of from about 3.3 to about 19.0 ml. per cubic foot. It will be obvious to those skilled in the art that the alcohol concentrations may be made higher if desired. It is contemplated that the concentrations as low as 1.0 ml. per cubic foot may be useful.

Again the examples herein illustrate the use of 10 or 15 grams of HCl with 500 ml. of methanol. While the process may be carried out without using an added catalyst, it is preferred to use from about 1 to about 10% by weight of an HCl catalyst, based on the weight of the methanol. Obviously higher amounts can be used, but are not preferred because of the resulting expense and slight corrosion problems with HCl gas.

The following examples serve to illustrate the method of heat treatment within the present invention, but it is understood that the examples are set forth merely for illustrative purposes, and many other variations of process for heat treatment are within the scope of the present invention.

EXAMPLE 1

Three portions of a coil of cold rolled steel were delivered to the annealing furnace approximately 2 to 3 months after rolling. The steel coils were relatively free from rust because of the oil film thereon. The steel weighed approximately 10 tons per coil portion, for a total of about 30 tons of steel. The coils were placed in a conventional annealing furnace of the box type, which was about 6 feet in diameter and about 10 feet high, with a sand seal about the outer periphery. The interior volume of the furnace was about 280 cubic feet. The steel occupied about 140 cubic feet or about 50% of the furnace volume. The furnace was purged with DX gas for two hours. The heating was commenced. About the time the DX gas temperature reached 150° during the anenaling heat cycle, one pint (about 500 ml.) of anhydrous methanol having about 15 grams of dry HCl gas dissolved therein, was released into the furnace. Two hours after the first methanol was released, as the DX gas temperature approached 450° F., an additional quart (about 1000 ml.) of methanol was released into the furnace. The conventional annealing process was then continued, with the furnace temperature being raised to about 1200° F. for approximately two hours, followed by conventionally cooling technique. The entire annealing process requires about 12 hours which is conventional.

The annealed coil was removed from the furnace to reveal an exceedingly bright and clean coil. It was classified as an enamel grade coil.

EXAMPLE 2

Three coils of cold rolled steel weighing a total of about 45 tons were placed in a conventional annealing furnace, as described in Example 1, and sealed with sand about the outer periphery. A bottle containing about one pint (500 ml.) of anhydrous methanol having about 15 grams of dry HCl gas dissolved therein and having a plastic cap thereon was placed in the furnace. A quart can containing about 1000 ml. of methanol was covered with a plastic cover and placed in the box anneal. The furnace was purged with DX gas for two hours. The heating was commenced. About the time the DX gas temperature reached 250° during the annealing heat cycle, the plastic caps melted, releasing the methanol and HCl. The conventional annealing process was continued, with the furnace temperature being raised to 1200° F. for approximately two hours, followed by conventionally cooling technique.

The annealed coils were removed from the furnace to reveal bright and clean coils.

EXAMPLE 3

A coil of cold rolled steel was delivered to the annealing furnace approximately 3 months after rolling. The steel coil weighed approximately 30 tons. The coil was placed in a conventional annealing furnace, as described in Example 1, and sealed with sand about the outer periphery. The furnace was purged with DX gas for two hours. The heating was commenced. About the time the DX gas temperature reached 150° during the annealing heat cycle, one pint (about 500 ml.) of anhydrous methanol having about 15 grams of dry boron trifluoride dissolved therein, was released into the furnace. The conventional annealing process was then continued, with the furnace temperature being raised to 1200° F. for approximately two hours, followed by conventional cooling technique.

The annealed coil was removed from the furnace to reveal a bright and clean coil.

In carrying out the method of the present invention it is necessary to consider the type of lubricant and the quantity of lubricant which is present on the material to be heat treated. In the cold rolling of steel products, various lubricants are used, some of which are proprietary.

However, the lubricants are generally used either in a simple mixture of oils and fatty acids or an oil in water emulsion wherein the oil comprises both mineral oil and fatty acids. Because of the mineral content of the water used in the emulsion, at least some of the fatty acids are generally converted into fatty acids soaps. Generally it is necessary to determine, either empirically, or by analytical testing, the average amount of such lubricants which are present based on the area of products being annealed. The minimum amount of methanol or other lower alkyl alcohols employed to carry out the process of the present invention will be dependent, proportionally, to the amount of lubricant present on the products being heat treated. However, as was mentioned above, excess amounts of methanol are not harmful.

It has been found that it is preferred to use a slight excess of the amount of methanol required, in order to produce a methanol concentration in the furnace high enough to insure complete esterification of all lubricants. While there is no real upper limit of the amount of methanol used, from a technical point of view, from a commercial point of view, the cost of methanol becomes excessive as the amount of methanol is increased above the quantity required by the lubricant. The present invention also contemplates that the anneal box should have a free volume which equals from about 20% to about 60% of the volume of the steel being heat treated. It is felt that the free volume assists the esterified lubricants in vaporizing and leaving the steel surfaces without leaving carbon snakes.

In carrying out the process of the present invention it is generally desirable to feed the lower alkyl alcohol to the annealing chamber after the purging step has been concluded, and as the heating is commenced. Preferably the alcohol is injected into the furnace when the temperature has reached a level which will insure volatilization of the alcohol. It is believed that the methanol-lubricant esterification reaction only occurs at elevated temperatures. It is generally desired to have the alcohol completely volatilized in order to distribute it uniformly throughout the annealing furnace and thus into the interstices of the coil or steel products being treated in order to react with all of the lubricant present thereon. While it is possible to add all of the methanol at one time in the annealing process, it is the preferred practice to add it incrementally over the heating cycle, such as when the temperature in the furnace is between 150° and 600° F. This enables the methanol to react with the lubricants at a temperature below the decomposition temperature of the lubricant, thereby permitting the lubricants to volatilize without decomposition and be carried away with the ventilated annealing gases. As is illustrated by Example 2, the methanol may be released into the anneal box by placing it in a container with a thermoplastic cover, which will melt as the desired temperature range is achieved.

As was mentioned above, it is possible to use any of several lower alkyl alcohols, such as alkyl alcohols containing up to about 5 carbon atoms, but it is preferred to use methanol. Methanol has the lowest volatility of the alcohols that is desired from that point of view. Further, the methyl esters which are formed by the reaction of the alcohol and the fatty acids have the lowest volatilization temperatures of the various esters which may be formed and the methyl esters thereby provide compositions which have a more pronounced tendency to volatilize rather than decompose or crack. Still further, methanol is preferred since it is commercially available at nominal prices.

The atmosphere within the annealing furnace during the heat treatment is not particularly critical with respect to the present invention. The examples illustrate the use of a conventional annealing gas, known as DX, which is produced by the partial combustion of methane and which has approximately the following composition:

	Percent
CO_2	5.9
CO	8.4
H_2	12.0
N_2	Balance

Other conventional annealing furnace gases such as HN, DEOX, or HNX may also be used interchangeably. It is necessary that the annealing furnace gas be substantially free from substances which tend to cause the oxidation of the lubricants or portions of the lubricants present on the surface of the steel members being heat treated. The process of the present invention may also be used with atmospheres of dry, pure nitrogen.

The process of the present invention may be used in any type of heating process or apparatus. For instance, conventional bell chamber or box annealing furnaces may be used, as well as other heating chambers known to those skilled in the art.

The forms of the invention herein shown and described are to be considered only as illustrative. It will be apparent to those skilled in the art that numerous modifications may be made therein without departure from the spirit of the invention or the scope of the appended claims.

I claim:

1. A method of heat treating steel products having lubricants thereon which comprises disposing the products to be heated in a heating chamber, introducing a controlled atmosphere into said chamber, introducing a lower alkyl alcohol containing up to about 5 carbon atoms into said furnace in a quantity sufficient to react with the lubricants on said steel products, heating said chamber to a temperature high enough to promote a reaction between said alcohol and said lubricant while ventilating said controlled atmosphere, continuing said heating and said ventilating whereby said lubricant-alcohol reaction products are volatilized and ventilated from said chamber.

2. A method of heat treating as described in claim **1**, wherein said alcohol is introduced in a plurality of increments.

3. A method of heat treating as described in claim **1**, whereoin said alcohol is methyl alcohol.

4. A method of heat treating as described in claim **1**, wherein an esterification catalyst is introduced to said chamber.

5. A method of heat treating as described in claim **4**, wherein said lower alkyl alcohol and said esterification catalyst are simultaneously introduced into said chamber.

6. A method of heat treating as described in claim **4**, wherein said esterification catalyst is selected from the group consisting of hydrogen chloride, and boron trifluoride.

7. A method of heat treating as described in claim **6**, wherein said esterification catalyst is hydrogen chloride.

8. A method of obviating carbon deposition on steel products during annealing, which products contain residual lubricants on the surface thereof, which process comprises surrounding said steel products with an atmosphere which includes lower alkyl alcohol vapors during the early stages of the heating process.

9. The method of claim **8**, wherein said alcohol is methanol.

10. The method of claim **8**, wherein said atmosphere includes a catalyst selected from the group consisting of hydrogen chloride and boron trifluoride.

11. A method of obviating carbon deposition on steel products during heat treatment, wherein said steel products have residual lubricants on the surface thereof, which comprises placing said steel products in a heating chamber, and during the early stages of the heating process, surrounding said steel products with an atmosphere which

includes an effective amount of a lower alkyl alcohol having up to 5 carbon atoms.

12. The method of claim **11** in which said alcohol is methanol.

13. The method of claim **11** wherein said atmosphere includes a catalyst.

14. The method of claim **13** wherein said catalyst is selected from the group consisting of hydrogen chloride and boron trifluoride.

15. The method of claim **12**, wherein the atmosphere includes from about 3.3 to about 19 milliliters of methanol per cubic foot of atmosphere.

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U.S. Cl. X.R.

148—16.7; 260—410.9 R