May 29, 1956 T. C. BURNHAM 2,748,037

METHOD OF TREATING ARTICLES REQUIRING ANNEALING

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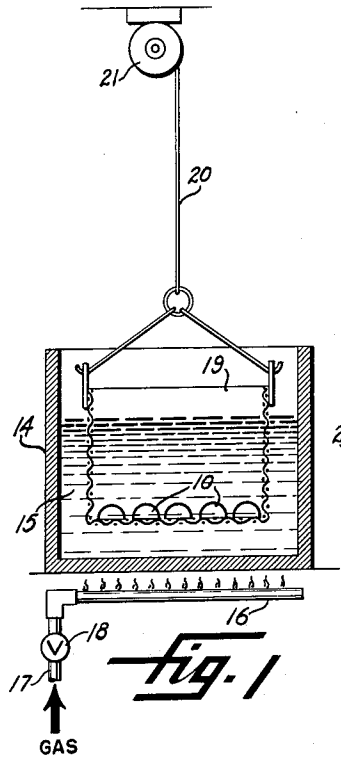


fig. 1

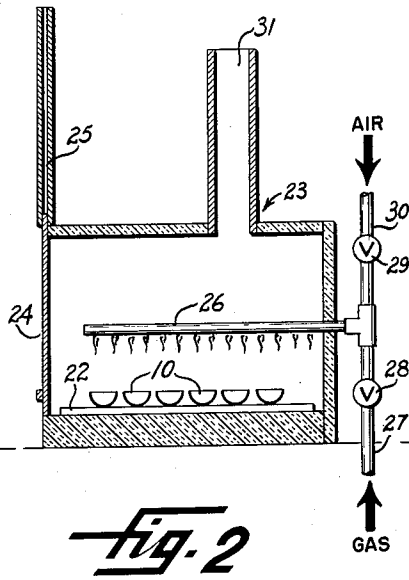


fig. 2

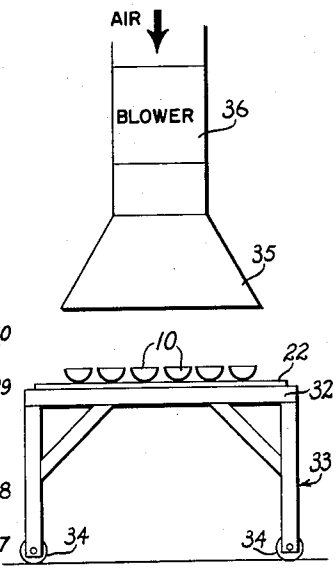


fig. 3

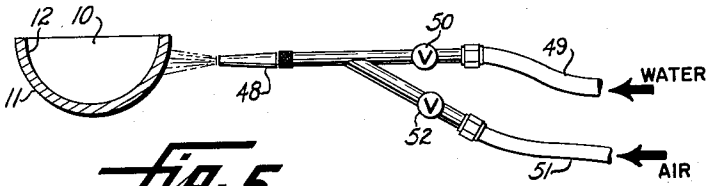


fig. 5

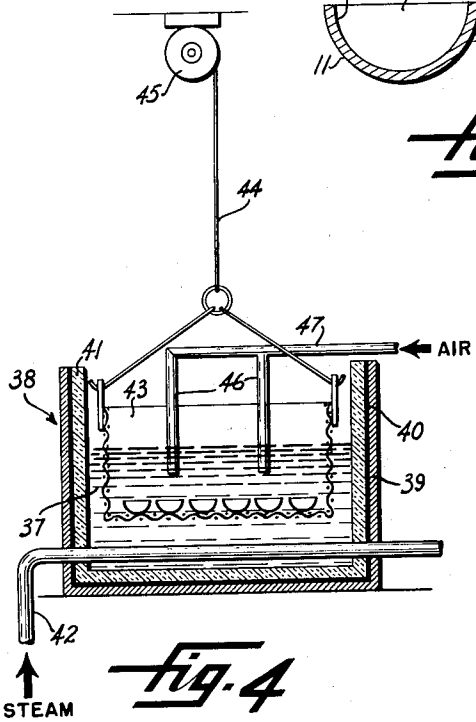


fig. 4

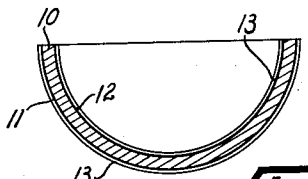


fig. 6

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METHOD OF TREATING ARTICLES REQUIRING ANNEALING

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This invention relates to a method for treating metal articles which require annealing. It is an object of the invention to provide a method which will prevent flaws on the surface of annealed metal articles after the scale incident to the annealing process is removed.

Another object is to provide a method for eliminating the deleterious effect which foreign material on the surface of certain metal articles has on their appearance, after they are annealed and the annealing scale removed.

Still another object is to provide a method for facilitating the removal of scale from stainless steel articles which require annealing without detracting from their appearance after removal of the annealing scale.

Further objects of the invention will become apparent as the description thereof proceeds. For a better understanding of the invention reference is made to the accompanying drawings, in which:

Figure 1 is a schematic view, partly in section, of apparatus used for coating the articles;

Figure 2 is a schematic view, partly in section, of a furnace used for annealing the articles;

Figure 3 is a schematic view of apparatus used for cooling the annealed articles;

Figure 4 is a schematic view, partly in section, of apparatus used for descaling the articles;

Figure 5 is a schematic view of apparatus for washing the articles, one of which is shown in cross section, and

Figure 6 is a sectional view of one of the articles.

In the manufacture of articles from corrosion and heat-resistant steels and other alloys, drawing and forming operations are often performed which harden the material and also induce large internal stresses in it. It is often found necessary to anneal such articles in order to relieve them of the internal stresses and condition them to be more easily formed in later operations. After the articles are treated to remove the scale formed on the surface during annealing, it is found that the surface does not have a uniform appearance but that some areas are more or less discolored and constitute blemishes on the annealed article. Any such blemishes constitute flaws in the article and adversely affect its saleability.

It has been found that such flaws result from two causes. The first is that the sheet stock from which the articles are cut and formed has a thin layer or shell on its surface which is harder than the material underneath and this shell is broken at many places where the article is bent during the forming operations. When the article is annealed, it is believed that oxides of somewhat different composition are formed at the areas where the shell is broken, then over the rest of the surface. When these oxides are later removed by a descaling solution, blemishes result from the differential action of the solution on the different oxides.

The second cause is the foreign material deposited on the surface of the articles during their manufacturing and handling. Such foreign material may cover the entire surface of an article or only some portions of the surface and may consist of dust particles raised from floor

sweeping, particles produced during grinding operations and floating about in the air, oil film and other material varying with the local surroundings.

It is believed that the presence of such foreign material on articles requiring annealing, causes the formation of different oxides in the regions covered by foreign material than in the clean areas and that after treatment by a descaling solution to dissolve the oxides and remove the scale, blemishes appear on the surface of the article at the areas where the foreign material was. It has been found by coating the articles with certain materials prior to their annealing that during the anneal heating the applied coating reacts with the foreign material and the surface of the article to form compounds which are entirely removed by the treatment later used to remove the annealing scale. A smooth, uniform surface texture is thus secured which has the same color shade throughout and is free of blemishes.

In the embodiment of the invention illustrated, each article **10** to be treated is shown of hemispherical shape and having exterior and interior curved surfaces **11**, **12** (see Figures 5–6). Each article has been previously blanked out from flat sheet metal and formed in a press to the desired shape. During this working of the metal, it is hardened and internal stresses set up in it, as above noted. It will be understood that this invention is not limited to the processing of articles of the shape illustrated but they may be of any shape whatsoever. Also, while each article is shown as a single piece of metal, the invention is not limited to such construction and an article may be formed of two or more pieces which are secured together by any known securing means. The foreign material above referred to is shown as a continuous layer **13** (see Figure 6) which covers the inside and outside of the article, however, this layer may be discontinuous and cover only a limited area or areas.

Coating

The application of a coating to the articles, which is an important feature of the invention, is effected in a tank **14** (Figure 1) containing a coating solution **15**. The tank is heated by a gas burner to maintain the solution at a temperature of preferably 80° F., the gas being supplied through a pipe **17** and regulating valve **18**. The articles to be coated are placed in a basket **19** whose bottom and sides are made of wire, perforated metal or other material which is chemically inert to solution **15**. The articles are not stacked up but arranged so that the solution has free access to every part of each article being coated. After being loaded, basket **19** is attached to a cable **20** and lowered into solution **15** by a power-driven winch **21**. After thorough wetting by the warm coating solution, basket **19** is raised by winch **21** to remove the articles and they are suspended above tank **14** for a short time to drain. They are then removed from the basket and are ready for annealing.

Typical austenitic steels on which my process has proved effective are listed below, the components being given in per cent by weight.

	Sample No. 1	Sample No. 2	Sample No. 3
Chromium	24 to 26	17 to 19	18 to 22.
Nickel	19 to 22	12 to 14	8 to 10.
Manganese	2.0 maximum.	2.0 maximum.	1.5 maximum.
Carbon	0.12 maximum	.08 maximum.	.36 maximum.
Molybdenum	0.50 maximum	2.0 to 2.5	1.00 to 1.75.
Copper	0.50 maximum	.50 maximum.	.50 maximum.
Tungsten	0 maximum	0	1.00 to 1.75.
Minor Constituents	.90 maximum.	1.07	1.40.
	Balance Iron.	Balance Iron.	Balance Iron.

One corrosion and heat-resistant alloy which is not austenitic and which has been successfully treated is:

Chromium 20%, nickel 20%, cobalt 20%, molybdenum 3%, tungsten 2%, columbium 1%, minor constituents 1.05%, balance iron.

Coating solutions which have proved effective have the following percentage compositions by weight:

Sample No. 1.—Sodium nitrate 43.5%, isopropyl alcohol 1%, sodium alkyl aryl sulfonate .06%, water 55.44%.

Sample No. 2.—Sodium carbonate 25%, trisodium phosphate 5%, sodium alkyl aryl sulfonate 0.25%, isopropyl alcohol 5%, water 64.75%.

Sample No. 3.—Trisodium phosphate 1%, phosphoric acid 10%, sodium alkyl aryl sulfonate 0.25%, isopropyl alcohol 5%, water 83.75%.

The sodium alkyl aryl sulfonate acts as a detergent and also to decrease the surface tension of the liquid thereby promoting the wetting of the surfaces of the articles being coated. Other suitable surface tension-reducing agents are isopropyl naphthalene sodium sulfonate and dioctyl sodium sulfosuccinate. The isopropyl alcohol promotes the rapid drying of the coating on the articles after their removal from the coating solution, and it will be understood that alcohols of different compositions may be used instead.

Annealing

Referring to Figure 2, the articles **10**, after coating, are placed on a steel tray **22** which is immediately put in an annealing furnace **23**. Dust and other particles floating about in the air of the factory are thus prevented from settling on them, as would be the case if they were permitted to remain exposed for a long time. The articles are not stacked together on tray **22** but are arranged so that the furnace gases circulate freely around them. At its front end, furnace **23** is provided with a door **24**, slidable in a vertical guideway **25**, the door being shown in its closed position. The interior of the furnace is provided with a gas burner **26** to which natural gas is supplied through a pipe **27** and control valve **28**, and air under pressure through a pipe **30** and control valve **29**. By using natural gas consisting chiefly of methane and small amounts of other hydrocarbons, it is easy to regulate the valves **28** and **29** so as to maintain a reducing atmosphere in the furnace. This may be checked by analyzing the burned gases issuing from the chimney **31**, a carbon monoxide content of 3% to 4% being satisfactory. The temperature in the furnace is controlled in accordance with the composition of the alloy being annealed, a temperature of about 2,050° F. being suitable for austenitic steels of the types above described. While the furnace illustrated is heated by gas, it will be understood that other sources of heat may be used instead. The heating is continued until the articles are fully annealed; in the case of the steels above described, a period of 2 to 3 minutes for each .010 inch of stock thickness being suitable.

It is thought that the alkali metal salt contained in the coating, reacts at the annealing temperature with the ash of the foreign material on the articles and with the oxides of their alloying elements to form compounds which are soluble in a descaling solution of the type described later herein.

Cooling

After annealing, the door **24** of the furnace is raised and tray **22** with the articles **10** thereon, removed from the furnace. The loaded tray is placed on a grating **32** which forms the top of a carriage **33** provided with supporting rollers **34**. Carriage **33** is rolled under a hood **35** to which a current of air at room temperature is supplied by a power operated blower or fan **36**. By this means the articles are rapidly cooled to room temperature and made ready for descaling.

Descaling

The descaling is effected by an acid solution **37** contained in a tank **38** which is open to the atmosphere. Tank **38** comprises a steel vessel **39** lined with an acid-resistant synthetic rubber lining **40** which is in turn covered with carbon brick as indicated at **41**. The solution **37** is heated to a temperature of between 160° F. and 180° F. by any suitable means, as by live steam passing through a heating coil or pipe **42** which passes through tank **38**, but electricity or other heat source may be used instead of steam. The annealed articles **10** are placed in a basket **43** made of wire or perforated metal which is not affected by solution **37** and the basket attached to a cable **44** wound about a power operated winch **45**. The winch is operated to lower the basket and articles **10** into the descale solution where they are permitted to soak until the scale is dissolved. The soaking period varies from 10 to 30 minutes or longer according to the nature of the scale and chemical composition of the articles. While the articles are soaking, solution **37** is kept well agitated by jets of air issuing from the lower ends of two or more pipes **46** to which air under pressure is supplied by a supply pipe **47**. This agitation keeps the sediment formed in the solution from settling on portions of the articles and thus preventing free access of the solution to such portions, a result which would interfere with uniform and rapid descaling. It also aids in dissolving and mixing chemicals added to keep the solution up to strength.

A descale solution found suitable for dissolving the scale of corrosion and heat-resistant stainless steels, and other chrome-nickel alloys has the composition by weight; 10 per cent ferric sulphate, 3.3 per cent hydrofluoric acid (free acid) and 86.7 per cent water. It is desirable to maintain a 3 to 1 ratio of ferric sulphate to hydrofluoric acid, therefore the solution should be tested at intervals and chemicals added to maintain the indicated strength and composition.

Washing

After soaking for a suitable length of time, the winch **45** is operated to raise basket **43** out of tank **38** and the basket is then lowered into a tank of water (not shown) which rinses the acid from articles **10** and removes a considerable portion of the loose scale. The basket and articles are then raised by winch **45** out of the rinse water and the articles removed from the basket. Usually some loose scale still adheres to the articles and to remove this entirely, each article is individually washed by a combined air and water spray issuing from a movable nozzle **48** (see Figure 5). Water is supplied to nozzle **48** through a flexible hose **49** and control valve **50**, and compressed air supplied through a flexible hose **51** and control valve **52**. After washing, the surface of the article has a uniform texture and color and is free of flaws such as discolorations and blemishes.

My invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. The present embodiment, as herein set forth, is therefore to be considered in all respects as illustrative and not restrictive, the scope of my invention being indicated by the appended claims rather than by the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

Having thus described my invention, what I claim as new and useful and desire to secure by Letters Patent is:

1. The method of annealing producing a smooth surface of substantially uniform texture and having the natural color of the alloy on a plurality of similar stainless steel articles formed to a curved shape and having internal stresses due to the forming, comprising the steps of wetting the entire articles simultaneously with an aqueous solution of a surface tension-reducing agent and a salt of the group consisting of sodium nitrate, sodium

carbonate and trisodium phosphate to form a coating on the articles; supporting the articles in spaced apart positions in a reducing atmosphere so that the entire coated surfaces of the articles are exposed to the reducing amosphere and simultaneously heating the coated articles to an annealing temperature; cooling the annealed articles simultaneously; immersing the articles simultaneously in a hot aqueous solution of ferric sulphate and hydrofluoric acid to dissolve the scale on the articles; and washing the articles to remove the dissolved scale.

2. The method of claim 1 comprising the additional step of forcing one or more streams of air into the hot aqueous solution while the articles are immersed therein.

3. The method of annealing curved stainless steel articles and removing a film of foreign matter from the surface of a plurality of similar stainless steel articles formed to a curved shape and having internal stresses due to the forming; comprising the steps of soaking the articles with the film thereon in an aqueous solution of a surface tension reducing agent and a salt of the group consisting of sodium nitrate, sodium carbonate and trisodium phosphate to form a thin coating on the articles; supporting the coated articles in spaced apart positions in a reducing atmosphere so that the entire coated surfaces of the articles are exposed to the reducing atmosphere and simultaneously heating the coated articles to an annealing temperature; cooling the annealed articles simultaneously; soaking the annealed articles simultaneously in a moving aqueous solution of ferric sulphate and hydrofluoric acid to dissolve the compounds formed by the film of foreign matter and the annealing scale with the coating on the articles; and washing the articles with water to remove the dissolved scale and permit the color of the alloy composing the articles to be seen.

4. The method of annealing and cleaning a plurality of curved stainless steel articles which are internally stressed and have an adherent dirt film on the surface thereof, comprising the steps of arranging the articles in spaced apart positions on a movable carrier so that each article is out of contact with adjacent articles; heating and aqueous solution of a surface tension-reducing agent and sodium nitrate; lowering the carrier with the separated articles thereon into the heated solution to provide a coating on the surface of each article; raising the carrier and the articles thereon out of the solution; supporting the carrier over the solution to permit excess coating on the articles to drain into the solution; removing the coated articles from the carrier; supporting the coated articles in spaced apart regions of a reducing atmosphere so that the entire surfaces of the articles

are exposed to the reducing atmosphere and simultaneously heating the coated articles to an annealing temperature; cooling the annealed articles simultaneously; and soaking the cooled articles simultaneously in a moving aqueous solution of ferric sulphate and hydrofluoric acid to dissolve the compounds formed by the film of foreign matter and the annealing scale with the coating on the articles.

5. The method of preparing a plurality of curved stainless steel articles which are internally stressed and have an adherent dirt film on their surface for forming, which comprises the steps of arranging the articles in spaced apart positions on a movable carrier; heating an aqueous solution of sodium carbonate about 25%, trisodium phosphate about 5%, alcohol about 5%, balance water to a temperature of the order of 80° F.; lowering the carrier with the separated articles thereon into the heated solution to provide a coating covering the surface of each article; raising the carrier and the articles thereon out of the solution; supporting the carrier and articles above the solution to permit excess coating on the articles to drain into the warm solution, removing the articles from the carrier; and annealing the coated articles.

6. The method of preparing a plurality of curved stainless steel articles which are internally stressed and have an adherent dirt film on their surfaces for forming, which comprises the steps of arranging the articles in spaced apart positions on a movable carrier; heating an aqueous solution of trisodium phosphate about 1%, phosphoric acid about 10%, alcohol about 5%, balance water to a temperature of the order of 80° F.; lowering the carrier with the articles thereon into the heated solution to provide a coating covering the surface of each article; raising the carrier and the articles thereon out of the solution; supporting the carrier and articles above the solution to permit excess coating on the articles to drain into the warm solution; removing the articles from the carrier; and annealing the coated articles.

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