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CLEANING CUPREOUS ARTICLES

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This invention relates to removing scale from cupreous articles by heating such articles in a halogen-bearing atmosphere and subsequently cooling them. Heretofore it has been necessary to introduce the halogen into the atmosphere by volatilizing a metal halide, as only indifferent results have been attained by introducing an elemental halogen or halogen acid directly into such atmosphere. We have now discovered that elemental halogens and halogen acids yield very satisfactory results when the atmosphere in which the articles are heated is substantially free of fuel combustion products, and the present invention is predicated on this discovery.

United States Patents Nos. 2,291,201 and 2,291,202 to W. H. Bassett, Jr., C. J. Snyder and W. G. MacLelland describe processes for cleaning cupreous articles by halogen treatment, thereby to remove the oxide scale that is always present on such hot-worked shapes as hot-rolled copper rods from which wire is drawn. The process of Patent No. 2,291,201 involves heating the cupreous article in a furnace atmosphere containing the vapor of a volatilizable metal halide, and thereafter cooling the article, preferably by quenching in water. The process of Patent No. 2,291,202 involves first dipping the article in an aqueous solution of a chloride, then heating the article in a furnace, and finally cooling the article, as by quenching. The process of the latter patent has been successful with hydrochloric acid as the solution in which the article is first dipped, thereby causing initial reaction of the acid with the article to take place in aqueous solution. Heretofore, however, it has not been feasible to use hydrochloric acid in the process of the former patent, by introducing it in gaseous form directly into the atmosphere in which the article is heated, because very unsatisfactory results have been attained by so doing. The processes of both of these patents have been used successfully, but that of Patent No. 2,291,201 has commercial advantages, because no preliminary dipping of the article to be cleaned into a solution is necessary.

We have found that elemental halogens and halogen acids may be used in place of the volatilizable metal halides described in Patent No. 2,291,201, for the purpose of establishing an effective halogen-bearing atmosphere within the furnace in which the cupreous article is treated, provided such atmosphere is substantially free of fuel combustion products (by "fuel combustion products" we mean the usual gaseous combustion products of ordinary carbonaceous and hydro-

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carbon fuels resulting from burning such fuels in air). Moreover, we have found that the use of these substances has distinct advantages that do not ensue from the use of a volatilizable metal halide. One such advantage is that when an elemental halogen or halogen acid is used, the article may be heated more rapidly and its treatment may be completed sooner than with metal halide vapors. Another advantage is that batch-type treatment of a weighed amount of the articles with a measured amount of the halogen or halogen acid is possible, resulting in closer control over the quality of the cleaning treatment.

In general, the present method for cleaning cupreous articles is similar to that described in Patent No. 2,291,201 and involves introducing the article to be cleaned, while it is substantially halogen-free, into a halogen-bearing atmosphere, heating it therein to a temperature of about 1250° F., and subsequently cooling it. In accordance with the present invention, however, the atmosphere in which the article is heated is maintained substantially free from fuel combustion products, and the halogen is introduced into said atmosphere by supplying directly thereto and in gaseous form a substance of the group consisting of elemental halogens and halogen acids.

When the halogen content of the atmosphere is provided by vapor from a volatilizable metal halide as described in Patent No. 2,291,201, most effective cleaning is accomplished by heating the article at the rate of about 50° F. per minute from room temperature to about 700° F., so that the article is held for a total time of twelve to fifteen minutes at a temperature below 700° F. The need for initial heating at this rather low rate evidently is required to allow for some of the vapor to collect on the article and react initially with its oxide scale, and with metal halide vapor such reaction appears to occur most effectively at a temperature in the range from 500° F. to 700° F. We have found that when an elemental halogen or halogen acid is used in place of a volatilizable metal halide to supply the halogen content of the treatment atmosphere, the time of heating at a temperature below 700° F. need be only two to five minutes, and such heating may be at a considerably lower temperature—down to 300° F. Consequently, about ten minutes or so may be saved in the time required for treating the article, and furnace equipment of given size can be made to handle a correspondingly greater amount of cupreous articles per day.

We believe the reason why the use of elemental halogens and halogen acids permits of more rapid treatment than the use of volatilizable metal halides is that these substances are highly reactive at temperatures much lower than that at which most metal halides yield substantial quantities of vapor. When the halogen is supplied as a metal halide vapor, an appreciable length of time is required for an effective amount of it to accumulate on the article and to undergo the reaction that initially takes place, but when an elemental halogen or halogen acid is employed, such reaction takes place so rapidly that a prolonged period of heating is not necessary. As stated above, however, it is necessary that the atmosphere in which treatment with an elemental halogen or halogen acid is carried out be substantially free of fuel combustion products. If the cupreous article is heated in a direct fuel-fired atmosphere, very unsatisfactory results are obtained by using an elemental halogen or halogen acid, although, for some reason that we are unable to account for with certainty, metal halide vapors are effective even in the presence of fuel combustion gases.

Another advantage found to result from the use of elemental halogens and halogen acids in lieu of volatilizable metal halides is that batch-type cleaning operations can be employed, using a measured amount of the halogen or halogen acid to treat a known weight of cupreous articles. When a volatilizable metal halide is employed, it is not feasible to measure the amount of metal halide vapor that is used to treat any given quantity of articles. Consequently, closer control over the cleaning operation is possible by using an elemental halogen or halogen acid in accordance with the present invention than when a volatilizable metal halide is employed.

The elemental halogen or halogen acid is introduced in gaseous form into the atmosphere in which the cupreous article is treated. The halogens that are not normally gaseous (bromine and iodine), and halogen acids that are used in aqueous solution, are rendered gaseous by vaporizing them, and the vapor is introduced into the treatment atmosphere. Vaporization may be accomplished outside the oven or furnace in which treatment takes place, and the vapors may then be led into the oven or furnace; or a measured quantity of the substance may be introduced directly into the furnace and may there be vaporized into the treatment atmosphere.

Following are examples of ways in which the method of the invention may be carried out:

Example 1.—A known weight of hot-rolled copper rods, having a scale composed mainly of cuprous and cupric oxides, is introduced into an electrically heated muffle-type furnace, and therein is heated as rapidly as the furnace permits to a temperature of about 1250° F. During at least the initial part of this heating, before the rods have attained a temperature of 700° F., a small stream of chlorine gas is flowed into the furnace atmosphere. The rate of flow of the chlorine, and the length of time for which it flows, are correlated with the amount of rods being treated to convert at least 1%, and preferably from 1% to 2%, by weight of the rods to an easily removed scale (scale formation to this extent has been found desirable for optimum cleaning). The flow of chlorine may be continued throughout the entire period of the heating operation, but it is preferable to introduce

it all, or nearly all, during the period that the rods are below 700° F. After the rods have reached a temperature of 1250° F., they are removed from the furnace and cooled to room temperature. Cooling may be in any manner desired, as pointed out in Patent No. 2,291,201, but generally it is convenient and most satisfactory to quench the rods in water. When the rods have cooled, a flaky scale peels readily and completely from them, leaving a clean unoxidized metal surface of excellent quality for wire-drawing.

Example 2.—A charge of hot-rolled copper rods, of known weight, is introduced with a measured quantity of iodine crystals into an oven heated to a temperature in the range from 300° F. to 700° F. The iodine quickly vaporizes at this temperature. The oven may be heated electrically, or may be indirectly heated by a fuel flame, but in any event the oven atmosphere is free of fuel combustion gases. The rods are held in the heated oven atmosphere for two to five minutes, but it is not necessary that they become heated to the oven temperature. After two to five minutes in the oven they are transferred to a furnace in which they are heated rapidly to a final temperature of about 1250° F. The furnace may be entirely separate from the oven, or oven and furnace may be two parts of the same heating apparatus, arranged so that the rods may be transferred from one part to the other easily and quickly. The transfer to the furnace may be made immediately after the oven treatment, or the rods may be stored in the air and allowed to cool to room temperature after the oven treatment and before being transferred to the furnace. The furnace atmosphere may be free of iodine vapor or other halogen during the latter period of heating to 1250° F., and may contain substantial quantities of fuel combustion gases, as the preliminary oven treatment at temperatures below 700° F. has resulted in effective accumulation of iodine or other halogen on the rod surfaces and has caused the initial reaction to occur. After attaining a temperature of about 1250° F., the rods are withdrawn from the furnace and cooled as by quenching.

Each of the preceding examples is based on batch-type operation, in which a known weight of rods is treated with a measured quantity of halogen or halogen acid. As previously stated, this procedure has the advantage of giving close control over the extent to which the rods are attacked and the amount of scale formed. It is not necessary, however, that the method of the invention be carried out batch-wise. It is possible instead to employ a continuous-type furnace such as is described in Patent No. 2,291,201, and merely substitute an elemental halogen or halogen acid for the metal halide, provided the design of the furnace is such as to exclude fuel combustion gases from the atmosphere in which the copper rods or other cupreous articles are treated. Such a substitution results in making the process more rapid, as previously mentioned herein. If a continuous-type furnace is employed, and if a temperature gradient is maintained in the furnace as described in Patent No. 2,291,201, it is generally preferable to introduce the halogen or halogen acid in gaseous form into the cold end of the furnace, rather than into the hot end as is done with the metal halide. The elemental halogens and halogen acids react with the copper of the articles rapidly enough at a relatively low temperature so that

it is not necessary for these substances to be brought in contact with the rods at the maximum temperature of the furnace. Indeed, it is necessary that at least some preliminary reaction take place between the halogen and halogen acid and the rod or other article before the latter has been heated to above 700° F.

Following is a brief summary of the forms in which some of the halogens and halogen acids have been used in accordance with the invention, and an indication of the results obtained. In each case hot-rolled copper rods, black on account of the presence of an outer scale of cupric oxide, were the articles being treated. The initially cold rods were heated in a muffle-type furnace to a final temperature near 1250° F., and then were quenched in water. Heating was accomplished as rapidly as the furnace would permit, the temperature of the furnace atmosphere being about 1300° F.

(*a*) Chlorine gas was flowed into the furnace during the first five minutes of the heating cycle, about at the rate of one-half liter (at normal temperature and pressure) per minute per hundred pounds of rods. A very heavy scale was formed but the results were good.

(*b*) Chlorine gas was flowed in at the same rate as in (*a*), but for only the first three minutes of the heating cycle, with excellent results.

(*c*) Chlorine gas was flowed in continuously throughout the heating cycle at a rate of about one-tenth liter per minute. Good results were obtained.

(*d*) Iodine crystals, in the amount of about 1.2 grams per hundred pounds of rods, were introduced into the furnace with the rods. Excellent results were obtained.

(*e*) Liquid bromine, in the amount of about 1 cubic centimeter per hundred pounds of rods, was introduced into the furnace with the rods. Excellent results were obtained.

(*f*) About 100 cubic centimeters of substantially saturated bromine water per hundred pounds of rods was introduced with the rods into the furnace. Good cleaning was obtained.

(*g*) A slow stream of hydrochloric acid gas was flowed into the furnace during the initial part of the heating cycle. Good cleaning resulted.

(*h*) About 2 cubic centimeters of aqueous hydrobromic acid per hundred pounds of rods was introduced into the furnace along with the rods. Very good results were obtained.

(*i*) Approximately 10 cubic centimeters of a 20% aqueous perchloric acid solution per hundred pounds of rods was introduced with them into the furnace. Good cleaning of the rods followed. (This reagent must be used with care, as it is explosive.)

(*j*) About 15 grams of chlorosulphonic acid per hundred pounds of rods was introduced into the furnace with the rods. A very heavy scale formed, indicating that considerably more chlorosulphonic acid than was necessary had been used, but the cleaning of the rods was excellent.

The adverse effect of fuel combustion products on the course of the cleaning operation is evident from a number of tests. For example, in one test chlorine gas was introduced in the same manner as in paragraph (*c*) above, but in admixture with commercial city gas and an excess of air. The city gas burned as it entered the furnace with a blue flame, owing to the excess of oxygen. Under these conditions only a moderate and rather unsatisfactory degree of cleaning was obtained. In another similar test in

which an insufficient amount of air to burn all of the city gas was used, so that the fuel burned with a yellow flame, no cleaning resulted. Evidently the moderate cleaning in the first of these two tests was made possible by the dilution of the combustion gases, by the excess air, and by the presence of the oxygen of the excess air. When this excess of air was eliminated so that the combustion gases were relatively concentrated in the furnace, the cleaning action stopped. Similar results were obtained when the premixed city gas and air were introduced and burned within the furnace separately from the chlorine. When a flame of burning city gas and air was introduced into the furnace while treating copper rods therein with iodine introduced with the rods in the form of iodine crystals, the amount of scale formed and subsequently separated from the rods was too small to result in thorough cleaning.

The introduction of air into the furnace along with the halogen or halogen acid is advantageous rather than otherwise. Thus with chlorine gas, for example, better cleaning was accomplished when the chlorine is introduced in a stream of air, than when the furnace is fairly tightly closed and commercially pure chlorine alone is introduced into the furnace. The easily separated scale that forms as a result of the treatment seems to be an oxyhalide, and evidently its formation is favored by the presence of free oxygen in addition to the combined oxygen present in the tightly adhering initial scale of cuprous and cupric oxides.

It is evident from the data given above that only quite small quantities of halogens and halogen acids are required to produce good cleaning. Indeed, too large a quantity of any of these substances should be avoided in order to prevent an excessive loss of metal in the scale. In the case of black hot-rolled copper rods for wire-drawing (which are generally about ⅜ inch in diameter and have a heavy coating of cuprous and cupric oxides) the amount of scale removed should be from 1% to 2% of the weight of the rods. At least about 1% by weight of the rods must be removed to be sure of complete cleaning and preferably the amount is about 1.5% for optimum results. From 2 to 20 grams of the halogen or halogen acid per hundred pounds of cupreous articles is generally enough to form this amount of readily removed scale when the articles are black hot-rolled copper rods. Larger or smaller amounts of these substances, and a larger or smaller percentage of metal lost in the scale, will, however, be preferable when the article being treated has an appreciably different ratio of surface-to-volume than ordinary hot-rolled copper rods for wire-drawing.

We claim:

1. In a process for removing scale from a cupreous article involving heating the article in a halogen-bearing atmosphere and subsequently cooling the article, whereby scale separates readily therefrom, the improvement which comprises introducing the article while substantially halogen-free into an atmosphere that is substantially free from fuel combustion products and from metal halide vapors, introducing a halogen into said atmosphere by supplying directly thereto and in gaseous form a substance of the group consisting of elemental halogens and halogen acids, and heating the article in said atmosphere to a temperature of about 1250° F.

2. In a process for removing scale from a cu-

preous article involving heating the article in a chlorine-bearing atmosphere and subsequently cooling the article, whereby scale separates readily therefrom, the improvement which comprises introducing the article while substantially halogen-free into an atmosphere that is substantially free from fuel combustion products and from metal halide vapors, heating the article in said atmosphere to a temperature of about 1250° F., and introducing chlorine gas directly into said atmosphere at least during the initial stages of said heating.

3. In a process for removing scale from a cupreous article involving heating the article in a halogen-bearing atmosphere and subsequently cooling the article, whereby scale separates readily therefrom, the improvement which comprises introducing a batch of known weight of said articles into a furnace and rapidly heating the batch therein in an atmosphere substantially free of fuel combustion products and of metal halide vapors at least to a temperature in the range from 300° F. to 700° F., introducing into said atmosphere during such heating a substance of the group consisting of elemental halogens and halogen acids, said substance being supplied in gaseous form directly to the atmosphere in which the batch of articles is heated and being measured in amount relative to the weight of the batch of articles to yield at least about 1% of said weight of easily separated scale, and thereafter further heating the batch to about 1250° F. and then cooling it.

4. In a process for removing scale from a cupreous article involving heating the article in a chlorine-bearing atmosphere and subsequently cooling the article, whereby scale separates readily therefrom, the improvement which comprises introducing a batch of known weight of said articles into a furnace and rapidly heating the batch therein in an atmosphere substantially free of fuel combustion products and of metal halide vapors at least to a temperature in the range from 300° F. to 700° F., introducing chlorine gas directly into said atmosphere during such heating, the amount of chlorine gas being measured in amount relative to the weight of the batch to yield an amount of easily separated scale equal to at least about 1% of said weight, and thereafter further heating the batch of articles to about 1250° F. and then cooling it.

5. In a process for removing scale from hot-rolled copper rods involving heating the rods in a chlorine-bearing atmosphere and subsequently cooling them, whereby scale separates readily therefrom, the improvement which comprises introducing a weighted batch of rods into a furnace and rapidly heating the batch therein in an atmosphere substantially free of fuel combustion products and of metal halide vapors at least to a temperature in the range from 300° F. to 700° F., flowing a small stream of chlorine gas into said atmosphere during at least a part of the time of such heating, the rate of flow of the chlorine gas stream and the time of said flow being such as to introduce into the furnace atmosphere an amount of chlorine sufficient to convert from 1% to 2% by weight of the batch of rods to the form of easily removed scale, and thereafter further heating the rods to about 1250° F. and then cooling them.

6. In a process for removing scale from a cupreous article involving heating the article in a halogen-bearing atmosphere and subsequently cooling the article, whereby the scale separates readily therefrom, the improvement which comprises introducing the article into an oven and heating it therein in an atmosphere substantially free of fuel combustion products and of metal halide vapors at a temperature in the range from 300° F. to 700° F., introducing into the oven atmosphere during such heating a substance of the group consisting of elemental halogens and halogen acids, said substance being supplied in gaseous form directly to the oven atmosphere, transferring the article after such heating to a furnace and heating it therein to a temperature of about 1250° F., and then removing the article from the furnace and cooling it.

7. In a process for removing scale from a cupreous article involving heating the article in a chlorine-bearing atmosphere and subsequently cooling the article, whereby the scale separates readily therefrom, the improvement which comprises introducing the article into an oven and heating it therein in an atmosphere substantially free of fuel combustion products and of metal halide vapors at a temperature in the range from 300° F. to 700° F., introducing chlorine gas directly into the oven atmosphere during such heating, transferring the article after such heating to a furnace and heating it therein to a temperature of about 1250° F., and then removing the article from the furnace and cooling it.

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