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CORROSION RESISTING IRON AND STEEL

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This invention relates to low carbon irons and steels which, in the form of articles, are to be exposed during use to corroding conditions. It relates particularly to iron or steel articles which corrode more uniformly and possess longer life under corroding conditions than similar articles made heretofore.

For many years iron or steel articles of low carbon content have been made for use under corroding conditions. Those articles possessed the common characteristic of corroding nonuniformly, with resultant formation of pits which eventually developed into holes. The length of useful life of the articles was determined by the rapidity with which these holes were formed. Many efforts have been made to increase the life of such articles but, so far as we know, such efforts which were made by others have not been entirely satisfactory or particularly noteworthy.

Some of our efforts to lengthen the useful life of such articles are set out in our prior United States Patents Nos. 2,121,055, 2,121,056 and 2,121,057 in which are disclosed compositions which possessed the property of more uniform corrosion than had been attained theretofore, so far as we are aware, and hence less tendency to localized pitting and the resulting formation of holes in the article. The greater uniformity obtainable by the compositions of the foregoing patents was traceable in part to the presence of phosphorous, aluminum and titanium, and arsenic and nickel respectively. We have now discovered that it is possible to make low carbon iron or steel articles which possess increased length of life under corroding conditions without the addition of the elements relied on in the above mentioned patents.

We believe that the tendency of prior low carbon iron or steel articles to corrode nonuniformly with the formation of pits and holes is traceable to relatively large amounts of oxygen and relatively small amounts of nitrogen in the molten metal and to the presence of correspondingly large amounts of oxides and small amounts of nitrides in the articles. In commercial irons and low carbon steels made by the effervescing process the oxygen content ranges from about .035% to about .09% and the nitrogen content ranges from about .003% to about .006%. Moreover, as the carbon content decreases the oxygen content increases and this is particularly noticeable when the carbon content is below about .07%. When aluminum, titanium, silicon and zirconium or manganese are added to such irons or steels as deoxidizers, oxides are formed which remain as segregated nonmetallic inclusions in the metal and which are apparently conducive to nonuniformity of corrosion and the formation of pits and holes.

We have found that when the oxygen content of such irons or steels is kept below .03% and, preferably below about .02%, and the nitrogen content is kept between about .007% and .2% and, preferably above about .085%, particularly when this is accomplished without the use of the ordinary deoxidizers, the articles made therefrom will corrode much more uniformly than has been the case heretofore, and will have correspondingly increased length of useful life under corroding conditions.

We have also discovered that low carbon irons or steels having nitrogen and oxygen contents within the ranges just stated and containing between about .15% and about 1.5% of copper have a greater elastic limit, tensile strength and hardness than, and about the same elongation as, the same irons or steels which contain lower amounts of nitrogen and higher amounts of oxygen. Similarly we have discovered that an iron or steel of the composition just described but additionally containing between about .05% and about .55% of molybdenum posses improvement of about the same order over irons or steels of the same composition which contain lower nitrogen and higher oxygen contents. We believe that these improved properties are traceable in part to the smaller amounts of oxides and higher amounts of nitrides in the articles.

Accordingly, the present invention is based primarily on the discovery that low carbon iron or steel articles which are to be exposed during use to corroding conditions can be improved in their physical properties and can be given much longer life if the nitrogen content ranges between about .007% and about .2% and the oxygen content is kept below .03% and preferably below .02%.

Articles embodying the present invention may have the following ranges in composition:

	Per cent
Iron	98 to 99.70
Carbon	.02 to .15
Sulphur	About .05 max.
Phosphorous	About .009–.04
Manganese	.01 to .50
Silicon	About .05 max.
Copper	.15 to 1.5
Nitrogen	.005 to .2
Oxygen	.03 max.

Molybdenum between about .05% and about .55% may also be included in the foregoing compositions.

A typical composition embodying the present invention is as follows:

	Per cent (about)
Iron	99.10
Carbon	.04
Sulphur	.035
Phosphorous	.009
Manganese	.17
Silicon	.005
Copper	.47
Nitrogen	.01
Oxygen	.015

When molybdenum is added to the foregoing typical composition it may be present in the amount of about .07%.

It is preferable that the contents of carbon, sulphur, phosphorous, manganese and silicon should not exceed about .25%. The preferred range of copper content is from about .4% to about .6% and the preferred range of molybdenum, when present, is from about .05% to about .35%.

The improvement in physical properties resulting from the present invention is indicated by the following table in which normalized, 16 gage sheets of substantially the typical composition above set forth and containing about .07% of molybdenum are compared with similar sheets of a similar prior art composition in which, however, the nitrogen content was about .0036% and the oxygen content was about .042%.

	Present composition	Prior art composition
T. S. lbs./sq. in.	57,560	50,100
El limit lbs./sq. in.	43,610	35,000
Percent elong. 2"	32	31
Hardness Rockwell "B"	66	61

When molybdenum was omitted from both of the foregoing compositions the foregoing physical properties were reduced somewhat but retained substantially the same order of improvement as is indicated by the following table:

	Present composition	Prior art composition
T. S. lbs./sq. in.	54,170	44,100
El. limit lbs./sq. in.	39,170	27,450
Elong. in 2"	29	33
Hardness Rockwell "B"	66	30

The corrosion resisting properties of articles of the present invention as compared with similar compositions of the prior art which, however, contained the lower nitrogen and higher oxygen contents of the order stated above, are indicated in the following table in which the figures express losses of metal in milligrams per square decimeter per day for the period tested.

	Present composition	Prior art composition
March–April, 1939		
314 hrs. partial immersion in aerated 6% H_2SO_4	222	358
314 hrs partial immersion in aerated 10% HCl	329	380
February–April, 1939		
1,000 hrs intermittent spraying with 3½% NaCl	35.1	70.2
July–August, 1939		
6 wks. exposure to pickling fumes	45.8	46.5
483 hrs. aerated 6% H_2SO_4	537	586
312 hrs. aerated 10% HCl	368	762
1,000 hrs. artificial sea w. spray	73.4	72.7
500 hrs. 3½% NaCl spray	135	125.2

Since H_2SO_4 corrosion is less pronounced in dry weather than in damp weather the March–April H_2SO_4 results are more nearly representative than those in the dry weather of July–August. The HCl results in dry weather are more nearly representative for dry weather favors corrosion by the chlorine. These results show strikingly the pronounced improvement achieved by the present invention, particularly when it is understood that heretofore decreases of a few percent in metal loss were considered important and some of the present decreases have approximated 50%.

Iron or steel articles of the present invention may be made by treating the molten metal in a furnace, in a ladle, or during pouring, with a suitable nitrogen containing compound which will liberate nascent nitrogen in the metal. An example of such material is calcium cyanamid. From about one pound to about five pounds of calcium cyanamid may be used. The nitrogen content of the metal apparently does not vary greatly with a variation in the amount of calcium cyanamid used, but the oxygen content decreases with increased amounts of calcium cyanamid up to about five pounds of the latter per ton of metal.

For example, when the molten metal was not treated with calcium cyanamid, articles of the above identified typical composition contained about .0531% of oxygen and about .0026% of nitrogen. When the metal was treated with about 2½ pounds of calcium cyanamid per ton of metal the articles had an oxygen content of about .0189% and a nitrogen content of about .0084%. When the metal was treated with about five pounds of calcium cyanamid instead of about 2½ pounds the articles had an oxygen content of about .0136% and a nitrogen content of about .0088%. When molybdenum was present to the extent of about .07% in the metal of the foregoing composition and the molten metal was not treated with calcium cyanamid, the oxygen content in the articles made from the metal was about .0420% and the nitrogen content was about .0036%. When the metal was treated with about four pounds of calcium cyanamid per ton, the oxygen content in the articles was about .0172% and the nitrogen content was about .0098%.

In the following claims the expression "the remainder being substantially all iron" and "the remainder being substantially all iron with small amounts of the usual impurities such as sulphur, phosphorous and silicon" include no molybdenum and also molybdenum up to about .55%.

Having thus described the present invention so

that others skilled in the art may be able to practice the same, we state what we desire to secure by Letters Patent is defined in what is claimed.

What is claimed is:

1. An iron article to be exposed during use to corroding conditions containing between about .02% and about .15% of carbon, between about .01% and about .5% manganese, between about .15% and about 1.5% of copper, between about .005% and about .2% of nitrogen, not more than about .03% of oxygen, the remainder being substantially all iron with small amounts of usual impurities such as sulphur, phosphorous and silicon.

2. An iron article to be exposed during use to corroding conditions containing between about .02% and about .15% of carbon, a maximum of about .05% of sulphur, a maximum of about .04% of phosphorous, a maximum of about .05% of silicon, between about .01% and about .5% of manganese, between about .15% and about 1.5% of copper, between about .005% and about .2% of nitrogen, a maximum of about .03% of oxygen, the remainder being substantially all iron.

3. An iron article to be exposed during use to corroding conditions containing above about .04% of carbon, about .035% of sulphur, about .015% of phosphorous, about .17% of manganese, about .005% of silicon, about .47% of copper, about .01% of nitrogen, about .014% of oxygen, the remainder being substantially all iron.

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