

**THE PROTECTION OF  
METALS FROM  
OXIDATION AT  
HIGH TEMPERATURES**

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The Protection of Metals from Oxidation at High Temperatures by William Ernst Ruder

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**WILLIAM ERNST RUDER**

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## HEAT COLORS

NAME	COLOR SCALE	CENT.	FAHR.
11 White		1204°	2200°
10 Light Yellow		1079°	1975°
9 Lemon		996°	1825°
8 Orange		941°	1725°
7 Salmon		899°	1650°
6 Bright Red		843°	1550°
5 Cherry or Full Red		746°	1375°
4 Medium Cherry		677°	1250°
3 Dark Cherry		635°	1175°
2 Blood Red		566°	1050°
1 Faint Red		482°	900°

NOTE—The above is a graphic suggestion of the relation between heat colors and temperatures. Such a scheme can be *only approximately* correct.





This brief review of some of the processes at present in use for protecting metals from oxidation will be confined to two types, firstly, that in which the metal itself is made more resistant, usually by some chemical treatment, and secondly, that in which another metal is used as a surface coating.

In the first instance a coating is formed which must possess the following properties, if it is to be successful: It must be homogeneous, continuous, resistant to attack by acids or alkali, firmly attached to the base metal and must have a similar expansion coefficient. The ideal metal coating should also be homogeneous and continuous, but should be strongly electropositive to the base metal and should form electropositive alloys with it, so that in case of oxidization the coating will be attacked and the base metal protected.

As iron is the metal most commonly used as the base, the processes chosen will be those used for its protection, although some may be applicable to other metals.

#### *Protection by Oxide Coatings:*

It was known for a considerable time before any process was devised that the black or magnetic oxide formed on iron, under certain conditions was a very fair protective coating. Attempts to control and improve this coating have led to a number of patented processes of which the following may be taken as typical.

#### *Bower-Barff Process:*

The pieces to be treated are heated to a temperature of 900 deg. C. in a closed retort. When this temperature has been reached, super-



heated steam is admitted for twenty minutes and a coating consisting of a mixture of red and black oxides is formed. Producer gas is then substituted for the steam and allowed to act for the same length of time. After cooling somewhat, the pieces are oiled and a smooth, green-black coating is produced, which affords efficient protection from sea water, acid fumes, etc., and will stand a wide variation in temperature.

#### *Gesner Process:*

This is a further development of the above process. The pieces to be treated are heated to a temperature of 900 deg. C in a closed retort; when this temperature has been reached, super-heated steam is admitted for twenty minutes after which steam at low pressure is let in at intervals for 30 minutes. The steam, on entering, passes through a red-hot pipe at the base of the retort, and is thus partially decomposed into hydrogen and oxygen. After this treatment, a small quantity of naphtha or hydrocarbon oil is introduced and allowed to act for fifteen minutes to reduce any red oxide, and also to carbonize the surface. The coating is said to be a compound of iron, hydrogen and carbon, and analysis has shown that a minimum of two per cent hydrogen is present. It is an improvement on the Bower-Barff process in that the danger of warping during the process is removed, since the treatment is carried out at lower temperature, and the tendency to scale is reduced for the same reason. Both processes are quite expensive.

#### *Protection by Chemical Means:*

There is one process which may be of interest in this connection, known after its inventor as "Coslettizing."

The pieces to be coated are first cleaned as usual, either by pickling or sand blasting, are then placed in a boiling water solution of phosphoric acid, in which iron or zinc filings are always present. The period of treatment is from one-half to three hours, depending on the thickness of the coating desired. After drying, the pieces are usually oiled. By this treatment a very slight amount of the surface of the article is converted into certain phosphates of iron, but most of the coating comes from the solution itself. This coating has been found to be particularly useful in the tropics, and is used in one instance for typewriters. It is, however, subject to patent restrictions.

#### *Protection by Another Metal:*

The agent used in the majority of cases for protecting iron is the metal zinc. Zinc is strongly electropositive to iron and so are its

alloys, if free from impurities. It is also readily available and may be applied by a number of processes.

#### *Hot Galvanizing:*

The oldest process is that of hot galvanizing, which consists simply of cleaning the pieces, coating with a suitable flux and then dipping in the molten zinc. The piece is usually wiped after this to improve the coating. This process has the disadvantage of limiting the thick corrosive substances in the coating, which may cause early failure.

#### *Cold Galvanizing:*

Another process which is being used more and more as it is improved is that of wet galvanizing or electroplating. In this case the article to be coated is suspended as a cathode in a suitable bath and is subject to easy control. It provides a coating of high purity and uniform thickness in general, but recesses and corners cause some trouble. It is liable to be more or less porous and may contain acid which will eventually cause failure. In both of these processes, hot or cold, the coating does not become intimately connected with the base metal through deep alloying.

#### *Lohman Process:*

A modification of this process is known as the Lohman Process. After cleaning, the article to be coated is dipped in the Lohman Bath, which is a solution of hydrochloric acid, mercuric chloride and ammonium chloride: it is then dried before immersing in the molten metal, which may be any one or a mixture of a number of metals such as lead, zinc and tin. The chief point in its favor seems to be that the junction between the iron and the protective alloy is kept free from all oxide, and, therefore, the alloy will fill all the pores and no corroding agent can be included.

It is claimed by its backers that a graduated alloy is formed so that the protective coating cannot be completely broken through except by breaking the sheet itself.

#### *Sherardizing:*

The latest process of this type is sherardizing. The object to be sherardized is placed in an iron drum which is filled with a mixture of finely powdered zinc and zinc oxide, in varying proportions, and is heated in a reducing or inert atmosphere for a period of time, the length of which depends on the thickness of coating desired. The coating so obtained consists of four protective layers. Next to the pure iron is an

alloy "C", rich in iron, upon which is another definite alloy "B", containing more zinc. Then there is a layer containing a number of more or less unknown alloys, and finally a layer of pure zinc. This makes a coating which is not easily broken down and which is continuous. The principal objections to its use are the high temperature to which the piece must be subjected and the increase in size which may be caused.

The theory which has been advanced to explain this process is interesting in that it may be considered as a distillation process. The zinc dust which is obtained from the zinc smelters is said to be in a state of unstable equilibrium, so that in contact with the hot iron it undergoes a change tending to restore it to the normal condition. During this change some of it alloys with the iron, thereby lowering the vapor pressure for zinc in that region. A slow distillation then begins from the zinc nearest the object itself. As the alloy becomes richer in zinc the difference in vapor pressure becomes less and less and then finally becomes zero. This is found to be the case in practice. The deposition becomes slower as the time is extended.

#### *Schoop Process:*

One of the recent processes is the Schoop Process. This is applicable to the deposition of metals or alloys on any sort of an object. The apparatus consists of a pistol into which the coating metal is fed as a wire. It passes through a straightening and centering device into the nozzles where it is fed through a burner whose temperature may be regulated from 700 deg. to 2000 deg. F. The molten metal is carried a short distance by the gas current and is suddenly caught by a powerful blast of compressed air which shoots it out of the nozzle with a velocity of 3000 feet per second, directly on the object to be coated, which is held a short distance away. The coating is continuous, and of any desired depth and is also exceedingly intimate. In the majority of cases it must be applied by hand.

#### *Calorizing:*

This recently developed process makes use of aluminum as the protective metal and is of particular advantage in preventing oxidation at high temperatures. The protective action is due to the oxide formed by the action of heat on the protecting metal, rather than to any electrolytic relations between the aluminum and the base. The product is distinguished from that of the foregoing processes in that they are intended primarily to give protection against oxidation at ordinary