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CASE HARDENING

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The present invention relates to the case hardening of metals and has particular reference to a novel case hardening bath and the method of operation thereof.

Case hardening baths have long been known and employed for imparting a surface hardness to iron and its alloys. A common method comprises treating the metal in a fused salt bath containing an alkaline earth metal salt to which case hardening properties are imparted by the addition of small amounts of a cyanogen compound, that is, quantities such that the bath is made to contain 1% or less of cyanide. In the practical application of this type bath, it has been found necessary for satisfactory results to utilize calcium chloride rather than other alkaline earth metal salts. As a consequence, the bath becomes hygroscopic and corrosive to adjoining metal surfaces. Corrosion of furnace parts, where it is excessive, necessitates frequent replacements. Operation is frequently made difficult by the precipitation of a sludge of calcium oxide which coats the work, gradually accumulates and settles to the bottom of the bath, and decreases the life of the melting pot. Extreme care is required in washing the case hardened work as otherwise rusting will occur. An acid dip is frequently required to remove the coating of lime from the work.

Furthermore, in operating a low cyanide bath of this type, it is obviously a difficult problem to retain the proper concentration of cyanide. The cyanogen compound must be added at relatively frequent intervals in order to maintain the case hardening activity at the required level. An excess of the activating agent in the bath will cause the formation of a sludge of carbon which coats the metal being treated and delays case hardening thereof.

According to prior art methods, a case hardening bath initially containing an appreciable quantity of an alkali metal cyanide may cease to operate with its original rapidity even before all of the cyanide has been decomposed. It has been implied that during the case hardening process the cyanide fosters the formation of products such as the oxide and carbonate of the base of the cyanide, which act to prevent further decomposition of the remaining original cyanide in the bath.

A principal object of this invention is the provision of an improved fused salt bath for case hardening metals, the activity of which is so regulated that it operates at a substantially uniform rate and retains its effective case hardening

action for an extended period of time. Another object is the provision of a molten bath for case hardening metals which is non-corrosive to surrounding equipment and which eliminates undue care in washing the case hardened parts. A further object of this invention is the provision of a case hardening bath of high fluidity which avoids the necessity of operating at temperatures which cause warping or distortion of the articles being treated.

These objects are accomplished by utilizing a fused salt bath containing a cyanide, substantially no calcium salts, and regulating the activity thereof by periodic addition of a substance as hereinafter more fully described.

In the practice of my invention, a case hardening bath is prepared comprising the following ingredients in substantially the following proportions:

	Percent
Sodium cyanide	30
Barium chloride	25
Sodium carbonate	23
Sodium chloride	11
Potassium chloride	11

The salts of equal particle size and free of moisture are thoroughly mixed together and fused in the furnace pot. Approximately $\frac{1}{8}$ of one per cent of graphite is added to inhibit decomposition of the salts on the surface of the bath, and also to decrease heat radiation losses from the surface.

I have discovered that superior case hardening results may be obtained by treating iron and its alloys in the above bath operated at temperatures between 1300° F. and 1650° F. However, I prefer to maintain the temperature at approximately 1550° F. Obviously the degree of case hardening is determined by the time and temperature employed. Therefore, the treatment may vary from approximately one minute to three hours.

When operating the above case hardening bath, I prefer to regulate the activity thereof and compensate for the loss of material caused by surface decomposition, by the periodic addition thereto of a substance designated as the activator comprising the following ingredients, in substantially the following proportions:

	Percent
Sodium cyanide	70
Barium chloride	18
Sodium chloride	6
Potassium chloride	5
Graphite	1

The activator is briquetted into cylindrical cakes or pellets weighing approximately 2 ounces each and added as such in an amount equivalent to $\frac{1}{16}$ to 2% of the weight of the bath per hour, that is, so as to maintain the NaCN content of the bath between 20 and 40%.

The sodium cyanide used in the preparation of the case hardening bath and the activator is a commercial grade containing approximately 90% pure sodium cyanide, although other grades may be used in place thereof.

The results shown in the following table were obtained by treating bars of S. A. E. X-1315 steel in the above described case hardening bath.

Temperature	$\frac{1}{2}$ hour	1 hour	2 hours
1500° F.-----	0.007" case..	0.012" case..	0.017" case..
1550° F.-----	0.009" case..	0.014" case..	0.021" case..
1600° F.-----	0.011" case..	0.016" case..	0.023" case..

The specific proportions of bath and activator as set out above may be varied somewhat and I have found that satisfactory results may be obtained within the following limits.

Case-hardening bath		Activator	
	Percent		Percent
NaCN -----	20-40	NaCN -----	50-75
BaCl ₂ -----	15-30	BaCl ₂ -----	15-30
Na ₂ CO ₃ -----	5-30	NaCl -----	5-20
NaCl -----	5-20	KCl -----	5-20
KCl -----	5-20	Graphite -----	5-2

In the commercial operation of a cyanide case hardening bath, losses will be incurred through two sources; first, chemical losses caused by decomposition of the cyanide through surface oxidation, by reaction with other bath constituents and by the reaction involved in treating the metal, and second, mechanical (drag out) losses caused by adherence of the molten bath material to the work when it is removed from the bath. Both of these losses must be compensated for if satisfactory operation over an extended period of time is to be maintained. In the past, materials have been added to compensate for mechanical drag out losses without provision being made for chemical losses. As a result, the chemical composition of the bath varies over a wide range producing non-uniform case hardening results. In my bath, the materials are so compounded that the activator and bath material are added to the bath to compensate for chemical and mechanical losses respectively. The activator, when added at regular intervals at a predetermined rate will compensate for chemical losses. The bath material which can be added at any time when needed, compensates for mechanical or drag out losses. Thus, the composition of my bath at any time during operation will be regulated within definite limits, as previously set forth. Variations in the amount of bath material necessary for replenishing drag out losses will not change the bath composition.

It is a fact that in a fused case hardening bath where the activator is solely or principally an alkali metal cyanide, substantially all of the sodium cyanide which decomposes eventually changes to sodium carbonate. I have found that the carbonate does not inhibit the dissociation of the original sodium cyanide, but that it actually causes an increase in the rate of decomposition thereof. This increased decomposition of the cyanide in the presence of large amounts of sodium carbonate does not add to the effective-

ness of the case hardening operation. The carbonate is soluble in the bath and oxidizing in action. It competes with the steel for the carbon which is liberated during the sodium cyanide decomposition, thereby reducing the amount of carbon available for carburization.

This objectionable effect is to a large extent avoided in my present bath in that a reaction takes place between the sodium carbonate and barium chloride. The barium carbonate which is thus formed is less oxidizing in action than the sodium carbonate and, consequently, will not react to as great an extent with the carbon liberated from the sodium cyanide decomposition. This leaves more of the atomic carbon formed from the dissociation of the sodium cyanide available for carburizing. As a result, the barium chloride gives rise to more efficient case hardening over wider ranges of sodium cyanide content. Moreover, it is believed that in spite of the fact that the vapor pressure of barium carbonate is in the neighborhood of 3 mm. at the operating temperature, effective quantities of barium cyanide are formed in the bath by reaction of the barium carbonate with NaCN. As alkaline earth metal cyanides are known to be good case hardening activators, the formation of such compound is entirely desirable. At any rate, better results are obtained with a bath made from barium chloride, sodium carbonate and sodium cyanide than one in which no alkaline earth metal cyanide can possibly exist. Alternatively barium carbonate may be added as such.

It will be thus observed that case hardening baths made up and operated according to the present invention will maintain a high degree of activity for an extended period of time. Corrosion of furnace parts and other miscellaneous equipment by the bath ingredients is avoided. Due to the high fluidity of the bath, the loss of the salt which adheres to the work when removed therefrom is exceedingly low, resulting in improved quenching conditions. Washing of the case hardened materials is greatly simplified, resulting in a saving of time, less handling and less washing equipment as compared to the washing of articles treated in case hardening baths known to contain calcium salts. Further advantages of my process in contrast to prior art methods are that it does not require as accurate control, as rigid supervision and is less sensitive to changes in operating procedures.

In the above specification, where "barium chloride" is referred to, it may be replaced in whole or in part by strontium chloride.

While the invention has been described with particular reference to specific embodiments, it is to be understood that it is not to be limited thereto, but is to be construed broadly and restricted only by the scope of the appended claims.

I claim:

1. The method of operating a molten bath for case hardening metals which initially included substantially 30% of sodium cyanide, 23.7% of barium carbonate, 11% of potassium chloride, the balance consisting of sodium chloride which comprises regulating the activity thereof by periodic addition of a mixture including substantially 70% sodium cyanide, 18% barium chloride, 6% sodium chloride, 5% potassium chloride and 1% graphite.

2. The method of operating a molten bath for case hardening metals which initially included sodium cyanide, barium carbonate, sodium chloride and potassium chloride which comprises reg-

ulating the activity thereof by periodic addition of a mixture including substantially 70% sodium cyanide, 18% barium chloride, 6% sodium chloride, 5% potassium chloride and 1% graphite.

3. The method of operating a molten bath for case hardening metals which initially included 20 to 40% of sodium cyanide, 9.2 to 28.4% of barium carbonate, 5 to 20% potassium chloride, the balance consisting of sodium chloride which comprises regulating the activity thereof by periodic addition of a mixture including substantially 70% sodium cyanide, 18% barium chloride, 6% sodium chloride and 5% potassium chloride and 1% graphite.

5 4. The method of operating a molten bath for case hardening metals which initially included 20 to 40% of sodium cyanide, 9.2 to 28.4% barium carbonate, 5 to 20% of potassium chloride, the balance consisting of sodium chloride, which comprises regulating the activity thereof by the addition thereto of a mixture including from 50 to 75% of alkali metal cyanide, 15 to 30% of a substance chosen from the group consisting of barium chloride and strontium chloride, the balance consisting principally of alkali metal chloride.

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