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PROCESS AND COMPOSITION FOR
TREATING METALS

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This invention relates to the treatment of ferrous metals and more particularly to methods and fused baths for cementation of ferrous metal articles and the products produced thereby.

5 A common method of cementation or introduction of hardness imparting elements such as carbon and nitrogen into the surface of ferrous metal articles comprises treating the articles in a bath of fused salts containing considerable
10 amounts of a cyanogen compound, for instance, an alkali metal cyanide. It has been also proposed to use for this purpose a salt bath containing an alkaline earth metal salt, to which case hardening properties are imparted by the addition
15 of small amounts of a cyanogen compound, e. g. such amounts that the bath is made to contain 1% or less of cyanide. Such a bath produces a cemented layer or case which is in general higher in carbon content and considerably lower in
20 nitrogen content than a case produced by salt baths containing 20% or more of alkali metal cyanide and no alkaline earth metal salts. In the practical application of this low cyanide type of bath it has been found necessary for satisfactory
25 results to use calcium chloride rather than other alkaline earth metal salts. Such a bath has a number of disadvantages, for instance, the calcium salt is hygroscopic and corrosive to metals; moreover, a sludge of oxide is precipitated in the
30 bath, making operation difficult and decreasing the life of the melting pot. The low cyanide bath has a relatively high rate of deterioration and the cyanogen compound must be added at relatively frequent intervals, usually several times
35 each day during an extended period of operation, in order to maintain the cementation activity at the required high level. For this reason it is difficult to obtain uniform cementation results because the activity of the bath tends to fluctuate
40 from a high stage when the cyanogen compound is added to a low stage just before the next addition is made.

An object of this invention is to provide an improved fused salt bath for the cementation of
45 ferrous metal articles, which bath contains alkaline earth metal salts, has a relatively low rate of deterioration, and may be satisfactorily operated below 900° C. without scumming. A further object is to provide a process whereby a superior
50 type of cementation case may be produced by treatment in a fused salt bath and a superior case on ferrous articles produced by this process.

These objects are accomplished by treating ferrous metal articles in a fused salt bath containing
55 considerable amounts of a fusible barium salt,

substantially no calcium salts, with or without small amounts of other alkaline earth metal salts and 10% or more of a metal cyanide.

We have found that baths utilizing less than 10% of metal cyanide are not satisfactory. Such
60 baths, when made active enough to produce satisfactory cementation have the disadvantage that a scum composed of carbon and possibly other materials is sometimes formed on the surface of the bath which sticks to the metal articles when
65 they are withdrawn. Furthermore, it is usually necessary to operate these baths with a high content of alkaline earth metal salt and a correspondingly low content of alkali metal salts. Consequently, the fusion points are high, so that,
70 unless these baths are operated at high temperatures, for instance, above 900° C., the viscosity of the melt may be too high for entirely satisfactory results. For these reasons these baths are not
75 satisfactory for the cementation of iron and steel articles at temperatures below 900° C. In certain cases it is highly desirable to case harden metals below this temperature in order to avoid distortion of the articles or other disadvantageous results incident to high temperature operation.
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We have discovered that superior cementation results may be obtained by treating ferrous metal articles in a fused bath containing a considerable amount, for instance, 30% or more of a barium salt, and 10% or more of sodium cyanide. The
85 presence of other alkaline earth metal salts tends to somewhat increase the activity of the bath but their presence is not essential for good results. If desired, another alkaline earth metal salt, for instance, a strontium salt, may be added to increase the activity of the bath, but its use should
90 be restricted to comparatively small amounts. We prefer to use barium chloride without the addition of any other alkaline earth metal salt.

Fused salt baths suitable for carrying out our
95 invention may be made by fusing barium chloride, alkali metal chlorides and sodium cyanide in such manner that the barium chloride content of the bath is preferably between 30% and 60%, and the sodium cyanide content is above 10%, preferably
100 between 10% and 20%. The purpose of the alkali metal chlorides is to lower the melting point so as to give the bath the desired degree of fluidity at the preferable operating temperatures; their concentrations are adjusted accordingly. Potassium
105 and sodium chloride are suitable for this purpose. Such baths may be operated at any desired temperature above the melting point. In general the best results are obtained at between about
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750° C. to 950° C.; however, we prefer to maintain the temperature during operation below 900° C.

The time of treatment according to this invention may vary from a fraction of a minute to a number of hours, depending on the results. Obviously, the degree of cementation is determined by the time and temperature of treatment. Lengthening the time of treatment has the effect of introducing more of the hardness imparting elements (i. e., carbon and nitrogen), and causing the production of a deeper case. The lower temperatures, in general, cause the formation of cases having relatively higher nitrogen content.

When operating a cementation bath having the herein described composition, we prefer to add fresh quantities of the original mixture only as necessary to replace the material which adheres to the treated articles when they are removed from the bath. For instance, in operating the bath described below in Examples 1 and 2, the treating vessel is kept filled by adding as needed a mixture having the approximate composition; 46% of barium chloride, 20% of potassium chloride, 17% sodium chloride and 17% of sodium cyanide. The rate of deterioration is so low that ordinarily by this mode of procedure the cyanide content of the bath is easily maintained above 10% and substantially uniform cementation is obtained over a period of at least one working day. If the cyanide content should fall below 10%, it is only necessary to additionally add a sufficient quantity of cyanide. This may be readily accomplished by adding to the bath once daily sufficient cyanide to bring the cyanide content of the bath up to 15-20%. For given operating conditions, the bath may be replenished by a mixture containing alkali metal chlorides, alkali earth chlorides, and alkali metal cyanide in such proportions as to maintain the bath activity at the desired level.

Example 1

A cementation bath was made by fusing a mixture consisting of 55% of barium chloride, 25% potassium chloride, and 20% sodium chloride and adding thereto about 20 parts by weight of sodium cyanide. The bath was heated to about 835° C. at which temperature analysis of a sample showed that the bath contained 14.25% sodium cyanide. After the bath had been used for cementation for 1 hour the cyanide content was 12.52%. Bars of S. A. E. 1020 steel were treated by immersion in the bath for one hour. After cooling, the cementation layer or "case" was analyzed by cutting successive layers of 0.004 inch each in depth from each bar by means of a lathe. Each layer thus cut from the bar was analyzed to determine the carbon and nitrogen content at the different depths of the case. The results are shown in the following table:

Layer of case	Carbon	Nitrogen
	Percent	Percent
Surface to 0.004 inch.....	0.70	1.09
0.004 inch to 0.008 inch.....	0.74	0.62
0.008 inch to 0.012 inch.....	0.49	0.24
0.012 inch to 0.016 inch.....	0.33	0.04

Example 2

A cementation bath was made up of the same composition as that described in Example 1, but was heated to 900° C. At this temperature the cyanide content of the bath was 17.34%. After

the bath had been operated for one hour at 900° C., the cyanide content was 16.58%. Bars of S. A. E. 1020 steel were treated in the bath for 1 hour at 900° C. and analyzed as described in Example 1. The results obtained were as follows:

Layer of case	Carbon	Nitrogen
	Percent	Percent
Surface to 0.004 inch.....	0.70	0.63
0.004 inch to 0.008 inch.....	0.79	0.45
0.008 inch to 0.012 inch.....	0.65	0.30
0.012 inch to 0.016 inch.....	0.42	0.13

In order to compare our invention with fused salt cementation processes used heretofore, we treated steel bars as described in Example 3 and with a typical cyanide bath containing no alkaline earth metal compounds and as described in Example 4 with a bath containing calcium chloride and less than 1% of cyanide.

Example 3

Bars of S. A. E. 1020 steel were treated at about 825° C. for one hour in a bath composed of about 20% sodium cyanide dissolved in a mixture of alkali metal chlorides and carbonates. The treated bars were cut and the case was analyzed as in Example 1. The following results were obtained:

Layer of case	Carbon	Nitrogen
	Percent	Percent
Surface to 0.004 inch.....	0.36	0.98
0.004 inch to 0.008 inch.....	0.27	0.42
0.008 inch to 0.012 inch.....	0.22	0.11
0.012 inch to 0.016 inch.....	0.16	0.01

Example 4

Bars of 1020 S. A. E. steel were treated for 1 hour at 860° C. in a bath containing about 82% calcium chloride, about 18% of alkali metal chloride and about 0.5% of sodium cyanide. Case depth analysis of a treated bar, carried out as described in Example 1 gave the following results:

Layer of case	Carbon	Nitrogen
	Percent	Percent
Surface to 0.004 inch.....	0.93	0.28
0.004 inch to 0.008 inch.....	0.72	0.21
0.008 inch to 0.012 inch.....	0.45	0.06
0.012 inch to 0.016 inch.....	0.28	0.01

Various combinations of salts and various methods of operation may be employed to carry out our invention without departing from the spirit and scope thereof. In place of sodium cyanide, other metal cyanides may be used, for instance, barium cyanide. Furthermore, part or all of the cyanide may be replaced by other cyanogen compounds or by substances which form cyanide when added to the bath. Other alkaline earth metal salts may be used in place of a barium salt, but they must be used in considerably smaller amounts. We prefer not to use substantial amounts of calcium and magnesium salts because of their corrosiveness to metals, their tendency to form insoluble oxides in the bath and because they make the bath too active for practical purposes.

By means of our invention, a superior type of cemented case, containing relatively high proportions of both carbon and nitrogen, may be produced. As may be seen from the above examples, 150

the case produced by our invention has a nitrogen content practically as high as that produced by the type of cyanide baths heretofore used. Furthermore, our case is superior to cases heretofore produced by cyaniding in the degree of nitrogen penetration and in the gradual transition from high to low nitrogen content.

A further advantage of our process is that it introduces a greater total amount of hardness imparting elements (carbon and nitrogen) into the metal and with deeper penetration than has been heretofore possible by fused salt bath treatment. The practical advantages of the case produced by the present invention will be apparent to those familiar with the treatment of metals. One such advantage is that the properties, such as wear resistance, of a case high in nitrogen are combined with the high strength and hardness of a carbon case.

Cementation baths made up and operated according to the present invention have a low rate of deterioration, and may be maintained at a sufficiently high degree of activity without adding activating agent or special salt mixtures. It is only necessary to add fresh quantities of the original bath mixture in amounts sufficient to compensate for the salt which adheres to the work removed from the bath. Hence, one salt mixture serves for both the original bath and addition agent.

The low rate of deterioration and the fact that the bath may be maintained at the desired activity by simply keeping the treating vessel filled with the salt mixture, insures that practically uniform cementation will be obtained over an extended period of operation without the necessity of making analyses and adding calculated amounts of activating agents and salts.

Good cementation results may be obtained by our process without the necessity of operating at temperatures which cause warping or distortion of the articles being treated. The fact that the herein described bath gives satisfactory cementation at comparatively low temperatures makes it especially suitable for the cementation of certain alloy steels which must be treated at or below 800°-825° C. to avoid material disad-

vantageous changes in the crystalline structure.

The bath herein described may be operated so that there is substantially no scum formation at temperatures between 800°-900° C., and little or no formation of material insoluble in the bath. The constituents of our bath are not hygroscopic and substantially not corrosive to ferrous metals.

We claim:

1. The process for cementation of ferrous metal articles comprising treating said articles in a fused salt bath consisting of 30-60% barium chloride, 12-20% sodium cyanide and 58-20% of salts of the group consisting of alkali metal chlorides and alkali metal carbonates.

2. The process for cementation of ferrous metal articles comprising treating said articles in a fused salt bath consisting of 30-60% barium chloride, 12-20% sodium cyanide and 58-20% of salts of the group consisting of alkali metal chlorides and alkali metal carbonates, said bath being maintained at 800-900° C.

3. The process for cementation of ferrous metal articles comprising treating said articles in a fused salt bath made by fusing together 46% of barium chloride, about 20% of potassium chloride, about 17% of sodium chloride and about 17% of sodium cyanide.

4. The process for cementation of ferrous metal articles comprising treating said articles in a fused salt bath containing about 46% of barium chloride, about 20% of potassium chloride, about 17% of sodium chloride, and about 17% of sodium cyanide, said bath being maintained at about 830° C.

5. A fusible mixture for the cementation of ferrous metal articles consisting of 30-60% barium chloride, 12-20% sodium cyanide and 58-20% of salts of the group consisting of alkali metal chlorides and alkali metal carbonates.

6. A fusible mixture for the cementation of ferrous metal articles comprising about 46% of barium chloride, about 20% of potassium chloride, about 17% of sodium chloride, and about 17% of sodium cyanide.

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