

UNITED STATES PATENT OFFICE

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TO AMERICAN CYANAMID COMPANY, OF NEW YORK, N. Y., A CORPORATION OF
MAINE

CASE-HARDENING METAL

No Drawing.

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This invention relates to the case-hardening of metals, such as articles of iron and steel for example, and has particular reference to those operations in which the case-hardening of the articles is effected by their immersion for a suitable period of time in a liquid bath of fused salts.

material over the surface of the calcium cyanamide, which causes it to lose a substantial percentage of activity and thus lessens its effectiveness in imparting case-hardening properties to the bath. Even the addition of fresh cyanamide does not procure the desired reactivation, since it also becomes coated with this inert and substantially impenetrable film.

It has been the common practice heretofore to make use of alkaline cyanides in compounding the ingredients of the liquid bath, these cyanides being used in conjunction with suitable alkaline chlorides and alkaline carbonates. However, serious disadvantages are attendant upon the employment of such cyanides, not only because of their higher cost, but also for the reason that they give off irritating gases and are very poisonous.

In Patents Nos. 1,279,457 and 1,279,458, both issued September 17, 1918, to Porter W. Shimer, one of the present applicants, there is described a molten bath containing such mixtures as calcium chloride and sodium chloride, potassium chloride and sodium chloride, and other similar compounds and mixtures, which, after being subjected to the action of calcium cyanamide immersed therein, acquire case hardening properties. The use of calcium cyanamide is particularly advantageous inasmuch as it is not poisonous, is readily obtainable at a moderate cost and is devoid of the objection of emitting irritating and dangerous gases upon immersion in a molten bath of salts, inasmuch as such gases as are evolved thereby burn at the surface of the bath and are non-poisonous and non-irritating. It has been found, however, that a case-hardening bath which has been used for a long time, especially under crude operating conditions, gradually loses its power of acquiring full case-hardening properties through the action of calcium cyanamide thereon. This loss of power to acquire full case-hardening properties is sometimes augmented by long continued use of the bath on a large-production scale, particularly when the articles being case-hardened are coated with scale or when cast iron pots are used to contain the bath. This deterioration of the bath is accompanied by the formation of a film of inert and relatively impenetrable

In Patents Nos. 1,518,607 and 1,532,663 issued December 9, 1924, and April 7, 1925, respectively, to Porter W. Shimer, one of the present applicants, there are described several methods of reactivating such deteriorated baths of fused salts. These methods consist in adding to the bath a reducing agent such as aluminum, or other active reagent such as sodium cyanide, both of which procure noticeable activity in the bath followed by the separation of dross, which may be removed from the bath by means of a perforated ladle. The removal of impurities in this manner fully restores the case-hardening properties of the bath, which remains so for a considerable length of time before the renewing process must be repeated.

While the processes described have been satisfactory heretofore, we have constantly endeavored to obtain a case-hardening bath which will continuously maintain uniform case-hardening strength without deterioration caused by the formation of impurities, or the decrease in strength of the compound which imparts the case-hardening properties to the bath. Another object of our experiments has been to provide a method of continuous uniform operation without stopping the process for the purpose of purifying the bath and renewing its case-hardening properties. The procurement of such a process of case-hardening metals, therefore, is the principal object of this invention, as well as the procurement of a case-hardening process which is more efficient, less expensive and requires fewer materials, operations or steps than those processes heretofore employed.

In accordance with the present invention, we have found that the regular and more or less frequent addition to a bath of fused salts of comparatively small amounts of a com-

pound containing the CN radical, has produced excellent case-hardening results. This regular addition of small amounts of CN-containing compounds cleanses the bath and maintains the case-hardening properties of the bath substantially constant, with the consequent procurement of a uniform depth and hardness of the case on the articles immersed therein. For example, instead of forming a cyanide in the bath as occurs when a cyanamide is added, a cyanide may be introduced directly in a fouled bath for the purpose of first removing the impurities and then imparting case-hardening properties to it. The conversion of the cyanamide in the bath to cyanide is accompanied by the slow accumulation of objectionable residues which are separated as dross by the next periodical addition of the CN containing compound.

We have obtained excellent case-hardening results by using such cyanides as sodium cyanide, or cyanide formed by the fusion of calcium cyanamide with sodium chloride, and which may be called "cyanamide cyanide". These cyanides are regularly and periodically added in minute proportions, such as $\frac{1}{4}\%$ of weight of bath, or $\frac{1}{2}$ ounce to a 15 pound bath, which may be formed by fusing dry sodium chloride and dry calcium chloride in proper proportions. While we have obtained good case-hardening results with the addition of as little as $\frac{1}{4}$ of one percent of the weight of the melt, we do not wish to limit ourselves to this small amount, and contemplate, when desirable, to use additions up to 1% of the weight of the melt. The exact amount and frequency of these cyanide additions naturally varies according to circumstances, such as the size of the bath, the shape of the pot, the temperatures used, the amount of work or articles to be case-hardened which are passed through the bath, the quantity of the bath removed by adherence to the articles upon removal, and the like. We have found that in a number of cases, the regular hourly additions of $\frac{1}{4}\%$ by weight of cyanide to the bath serve the most important purpose of keeping the strength of the bath constant throughout the day, with the consequent uniformity of depth and hardness of case. This regularity is impossible to obtain by use of the common cyanide mixtures containing high percentages of cyanide (20% to 96%), because of the rapid falling off of their cyanide strength after the bath has been in use for a short time.

The "cyanamide cyanides" may be formed by fusing calcium cyanamide, barium cyanamide, or any cyanamide of the alkaline earth metals, with suitable salts. As previously mentioned, a convenient "cyanamide cyanide" may be formed by fusing calcium cyanamide and sodium chloride together. If a bath such as dry calcium chloride and dry

sodium chloride, fused together, is used, calcium cyanide is largely formed when dry calcium cyanamide is added to such a bath. The cyanide formed in the molten calcium chloride-sodium chloride bath by the addition of calcium cyanamide is, no doubt, a calcium cyanide, for, years ago, we found that a fused bath of calcium chloride alone, in which calcium cyanamide is immersed, acquires case-hardening properties. Furthermore, finely granulated, anhydrous calcium cyanamide alone submerged in a bath of fused salts, in regular and periodic proportions closely approximating the procedure when using cyanides, also gives good case-hardening results, without the use of the usual submerged quantity of lump cyanamide. When otherwise unobjectionable, this granulated cyanamide may be added on top of the bath, which has the additional advantage of protecting the case-hardening elements of the bath from oxidation by the air; but it is preferred that this granular cyanamide be introduced beneath the surface of the bath by means of a perforated container. This regular addition of small quantities of cyanamide constantly maintains the full case-hardening strength of the bath, regularity in the depth and hardness of the case on the metal treated, while the case-hardening elements, carbon and nitrogen, are taken up in the bath, leaving an inert residue, which may be removed in its container.

The addition of cyanide-containing or cyanide-forming compounds in small but regular amounts to the case-hardening baths described in Patents Nos. 1,279,457 and 1,279,458, has the effect of considerably prolonging the life of the cyanamide previously immersed therein. In this way the period of effectiveness of the cyanamide is doubled and often trebled, while a uniform case is obtained on the articles immersed in the bath, due to a favorable interaction between the cyanamide and the cyanide which appears to occur.

It will be seen that the new process of case-hardening metals procures many advantages over the former methods, and particularly in that harder, deeper and more uniform cases may be obtained with greater economy and ease, and that the case-hardening bath retains its case-hardening properties more uniformly and for much longer periods than formerly by regularly adding to the bath of molten salts relatively small amounts of a dry compound containing the CN radical, such as sodium cyanide, calcium cyanamide, a "cyanamide cyanide", and the like. This bath comprises a dry, fused mixture of suitable salts to which is imparted case-hardening properties by these small but regular additions of CN containing compounds, or the bath may contain a case-hardening compound the activity of which is extended and

increased by these small but regular additions of CN containing compounds.

We claim:

1. The method of imparting and maintaining case-hardening properties to a molten bath of fused salts, which consists in regularly adding at frequent intervals relatively small amounts of a cyanide-forming compound.

2. The method of imparting and maintaining case-hardening properties to a molten bath of fused salts, which consists in regularly adding at frequent intervals relatively small amounts of a cyanamide.

3. The method of imparting and maintaining case-hardening properties to a molten bath of fused salts, which consists in regularly adding at frequent intervals relatively small amounts of calcium cyanamide.

4. The method of increasing and prolonging the case-hardening properties of a molten bath of fused salts containing a cyanamide, which consists in regularly adding at frequent intervals, relatively small amounts of a cyanide-forming compound.

5. The method of increasing and prolonging the case-hardening properties of a molten bath of fused salts containing a cyanamide, which consists in regularly adding, at frequent intervals, relatively small amounts of a cyanamide.

6. The method of increasing and prolonging the case-hardening properties of a molten bath of fused salts containing a cyanamide, which consists in regularly adding, at frequent intervals, relatively small amounts of calcium cyanamide.

7. The method of increasing and prolonging the case-hardening properties of a molten bath of fused calcium and sodium chlorides containing a cyanamide, which consists in regularly introducing at frequent intervals relatively small amounts of granular calcium cyanamide.

In testimony whereof we affix our signatures.

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