

UNITED STATES PATENT OFFICE

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METHOD OF STABILIZING ALKALI METAL
NITRATE MELTS USED IN THE HEAT
TREATMENT OF METALSJosef Martin Michel, Bitterfeld, Germany, as-
signor to I. G. Farbenindustrie Aktiengesell-
schaft, Frankfurt-on-the-Main, GermanyNo Drawing. Application July 10, 1937, Serial
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12 Claims. (Cl. 148—13.1)

This invention relates to a method of stabilizing saltpetre melts used in the heat-treatment of metals.

The heat-treatment of alloys, especially aluminium alloys, on a commercial scale, is usually effected with the aid of saltpetre baths. In order to obtain a melt of the greatest possible fluidity, even at comparatively low temperatures, the eutectic mixture (50/50) of potassium-nitrate and sodium nitrate, having a melting point of 218° C. is generally preferred. Working with these salts and mixtures thereof, however, is not free from danger, since, owing to circumstances as yet unknown in detail, nitrate baths tend to undergo sudden decomposition of an explosive character, when in use. In this connection, an important part is undoubtedly played by the ready tendency of fused alkali metal nitrates to decompose into alkali metal nitrite and oxygen, which may even lead to the formation of alkali metal oxide. It is also known that, within the working temperature range of about 200 to 500° C. nitrate melts attack the iron vessels, and also the work-pieces under treatment. With the object of preventing such corrosion of the metal parts coming into contact with the saltpetre bath, it has already been recommended to add up to 2% of an alkali metal chromate, or dichromate, to the saltpetre melts. Whilst such an addition, which apparently establishes a superficial passivation of the metal articles, prevents reaction between the saltpetre melts and the material, experience has shown that it does not obviate the sudden decomposition of the nitrate melts above referred to.

It has now been ascertained in accordance with the present invention, that decomposition of the baths is reliably prevented by the addition of an alkali-, or alkaline-earth metal monochromate in quantities exceeding 2% to fused saltpetre baths, whereas an addition of dichromates alone is ineffective for this purpose.

A similar, though less pronounced, effect is produced by an addition of alkali or alkali earth metal tungstates, molybdates, vanadates and manganates.

Based on the foregoing observations the present invention provides a process for stabilizing heat-treatment baths, with a basis of saltpetre, which comprises adding to the bath an alkali monochromate in a quantity exceeding 2% of the bath and depending on and increasing with the working temperature of the bath. Thus, it has been found that the proportions of K_2CrO_4 required for stabilizing saltpetre baths at a work-

ing temperature of 300° C. are between 2 and 5%; for 400° C. between 5 and 10%; and for 500° C. between 10 and 20%. The same proportions, depending on the temperature, apply, when instead of alkali metal monochromate, the corresponding tungstate, molybdate, vanadate or manganate compounds are employed.

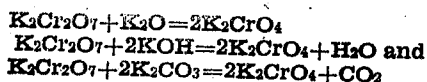
The following table, which specifies the nitrite content and the alkalinity (due to the formation of K_2O)—both being representative of the progressive decomposition of the bath—in a fused eutectic mixture of potassium- and sodium nitrate, at a working temperature of 500° C. ascertained after varying periods of employment of the bath, clearly shows the stabilizing effect of an addition of monochromate in accordance with the invention.

Period of use, days	Without addition of chromate		With addition of 10% of chromate	
	N_2O_5 , percent	Alkalinity, grm. n/10 HCl	N_2O_5 , percent	Alkalinity, grm. n/10 HCl
1.....	0.17	0.12	0.17	0.10
2.....	0.33	0.21	0.18	0.11
3.....	0.56	0.32	0.20	0.13
6.....	3.60	2.40	0.18	0.09
30.....	12.45	14.65	0.18	0.12

It has further been observed that the baths stabilized in accordance with the present invention still exhibit a certain small residual alkalinity which is attributable to a moderate reaction of the saline melt with the work-pieces to be treated and also with any oil or other carbonaceous matter superficially adhering thereto, and which alkalinity, although insufficient in itself to cause corrosion of the aluminium alloys under treatment, nevertheless may be objectionable, because it is liable to produce a discolouration on the surface of the treated material; moreover, on dissolution of the salt still superficially adhering to the treated workpieces in water used for subsequent quenching the latter becomes increasingly alkaline and may give rise to similar phenomena.

This residual alkalinity of the melts, irrespective as to whether it is due to alkali metal oxide, hydroxide or carbonate, can, in accordance with the present invention be avoided without impairing the other favourable properties of the baths, by further adding to the melts containing monochromate in the above proportions such an amount of alkali metal dichromate that the free alkali still remaining in the melts (which is ascertainable by the usual methods of analysis, e. g., by determining the pH value of a 5% aqueous

solution of a sample of the saline melt) is transformed into monochromate, in accordance with the equations:



An excess of alkali metal bichromate should, however, be carefully avoided, since it would lead to decomposition phenomena in the melts.

The following examples are representative of the procedure to be followed in removing the residual alkalinity from baths according to the invention.

Example I

5000 kgs. of a saline melt consisting of a mixture of equal parts by weight of potassium nitrate and sodium nitrate and containing in addition 3.66% of sodium monochromate, after having been used for a fortnight for the treatment of aluminium base alloys at temperatures between 310 and 320° C., were found to have a residual alkalinity of 0.15%

$$\left(\frac{\text{K}_2\text{O} + \text{Na}_2\text{O}}{2} \right)$$

Accordingly, an addition of 29.5 kgs. of potassium bichromate was made to this bath, whereupon after two hours, free alkali was no longer ascertainable in the melt.

Example II

12,000 kgs. of a saline melt consisting of equal parts by weight of sodium and potassium nitrate and in addition 6.74% of sodium monochromate which had, for the purpose of heat-treating aluminium alloys been in use for a period of three weeks at temperatures between 320 and 330° C., were found to have acquired a residual alkalinity of 0.28%

$$\left(\frac{\text{K}_2\text{O} + \text{Na}_2\text{O}}{2} \right)$$

In order to remove such residual alkalinity 132 kgs. of potassium bichromate were added to the melt, samples of which, taken after four hours, showed a completely neutral reaction.

The residual alkalinity of the melts according to the present invention should be tested from time to time and re-adjusted to zero by corresponding additions of bichromate.

Seeing that even a local supersaturation of the melt with dichromate would result in a decomposition of the nitrates present, it is advisable to incorporate the requisite amount of dichromate with the melt, conjointly with the addition of monochromate, by previously intimately mixing the monochromate and dichromate in the required relative proportions.

Although it might seem feasible, the use of chromic acid in place of dichromate, has been found to be impracticable, since the chromic acid undergoes decomposition under the temperature conditions obtaining.

For the purposes of the present invention, the alkali metal compounds to be added to the nitrate baths may be replaced by similar proportions of the corresponding salts of the alkaline earth metals provided their limit of solubility in the nitrate baths is not exceeded.

I claim:

1. A method of stabilizing saltpetre melts for use in the heat-treatment of alloys, which comprises adding to such melt at least one substance of the group consisting of alkali- and alkaline-

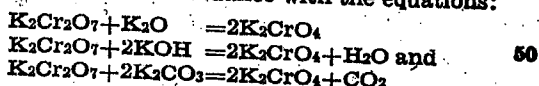
earth metal mono-chromates, molybdates, tungstates, vanadates, and manganates, in a quantity exceeding 2% but not exceeding about 20% of the weight of the melt, such quantity increasing within the range specified as the temperature of operation of the melt increases within the range from about 250 to about 550° C.

2. A process of stabilizing saltpetre melts for use in the heat-treatment of alloys at temperatures between about 250 and 350° C., which comprises adding to such melt at least one substance of the group consisting of alkali- and alkaline-earth metal mono-chromates, molybdates, tungstates, vanadates, and manganates in an amount ranging between 2 and 5% of the weight of the melt.

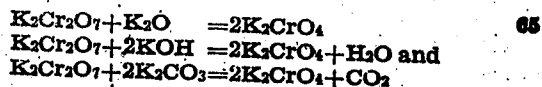
3. A process of stabilizing saltpetre melts for use in the heat-treatment of alloys at temperatures between about 350 and 450° C., which comprises adding to such melt at least one substance of the group consisting of alkali- and alkaline-earth metal mono-chromates, molybdates, tungstates, vanadates, and manganates in an amount ranging between 5 and 10% of the weight of the melt.

4. A process of stabilizing saltpetre melts for use in the heat-treatment of alloys at temperatures between about 450 and 550° C., which comprises adding to such melt at least one substance of the group consisting of alkali- and alkaline-earth metal mono-chromates, molybdates, tungstates, vanadates, and manganates in an amount ranging between 10 and 20% of the weight of the melt.

5. A method of stabilizing saltpetre melts for use in the heat-treatment of alloys, which comprises adding to such melt at least one substance of the group consisting of alkali- and alkaline-earth metal monochromates, molybdates, tungstates, vanadates, and manganates, in a quantity exceeding 2% but not exceeding about 20% of the weight of the melt, such quantity increasing within the range specified as the temperature of operation of the melt increases within the range from about 250 to about 550° C., and also an amount of alkali metal dichromate sufficient to convert the free alkali present in the melt into monochromate in accordance with the equations:

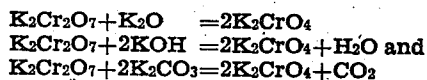


6. A process of stabilizing saltpetre melts for use in the heat-treatment of alloys at temperatures between about 250 and 350° C., which comprises adding to such melt at least one substance of the group consisting of alkali- and alkaline-earth metal mono-chromates, molybdates, tungstates, vanadates, and manganates in an amount ranging between 2 and 5% of the weight of the melt, and also an amount of alkali metal dichromate sufficient to convert the free alkali present in the melt into monochromate in accordance with the equations:



7. A process of stabilizing saltpetre melts for use in the heat-treatment of alloys at temperatures between about 350 and 450° C., which comprises adding to such melt at least one substance of the group consisting of alkali- and alkaline-earth metal mono-chromates, molybdates, tungstates, vanadates, and manganates in an amount

ranging between 5 and 10% of the weight of the melt, and also an amount of alkali metal dichromate sufficient to convert the free alkali present in the melt into monochromate in accordance with the equations:



ceeding 2% but not exceeding about 20% by weight of the saltpetre, such quantity increasing within the range specified as the temperature of operation of the melt increases within the range from about 250 to about 550° C.

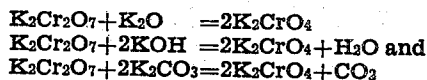
10. A saline melt for use in the heat-treatment of metals at temperatures between about 250 and 350° C., substantially consisting of saltpetre and containing between 2 and 5% by weight of the saltpetre of at least one substance of the group consisting of alkali- and alkaline-earth metal monochromates, molybdates, tungstates, vanadates, and manganates.

11. A saline melt for use in the heat-treatment of metals at temperatures between about 350 and 450° C., substantially consisting of saltpetre and containing between 5 and 10% by weight of the saltpetre of at least one substance of the group consisting of alkali- and alkaline-earth metal monochromates, molybdates, tungstates, vanadates, and manganates.

12. A saline melt for use in the heat-treatment of metals at temperatures between about 450 and 550° C., substantially consisting of saltpetre and containing between 10 and 20% by weight of the saltpetre of at least one substance of the group consisting of alkali- and alkaline-earth metal monochromates, molybdates, tungstates, vanadates, and manganates.

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8. A process of stabilizing saltpetre melts for use in the heat-treatment of alloys at temperatures between about 450 and 550° C., which comprises adding to such melt at least one substance of the group consisting of alkali- and alkaline-earth metal monochromates, molybdates, tungstates, vanadates, and manganates in an amount ranging between 10 and 20% of the weight of the melt, and also an amount of alkali metal dichromate sufficient to convert the free alkali present in the melt into monochromate in accordance with the equations:



9. A saline melt for use in the heat-treatment of metals, substantially consisting of saltpetre and containing at least one substance of the group consisting of alkali- and alkaline-earth metal monochromates, molybdates, tungstates, vanadates, and manganates in a quantity ex-