# UNITED STATES PATENT OFFICE

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#### ALLOY ADDITION AGENT

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The invention relates to a method and agent for incorporating alloying elements into molten iron or steel and for adding heat to molten iron and steel to facilitate the addition of alloying elements to such metals.

It is well known that the addition of ferro-alloys such as ferrochromium to steel or cast iron can be greatly facilitated by incorporating with the ferro-alloy an exothermic mixture which, upon addition to molten iron or steel, will react, liberating heat. This heat raises the temperature and heat content of the ferro-alloy, thereby reducing the chilling effect that normally accompanies the addition of such alloys to molten iron or steel. The advantages of these exothermic liberation have long been recognized by those skilled in the steelmaking art.

Customarily, these agents are prepared by pelleting or briquetting intimate mixtures of finely comminuted fero-alloy, a reducing agent, and an 20 oxidizing agent. The reducing agent may be added separately or may be a component of the ferro-alloy. The pellets or briquets may be bonded in any of a number of different ways depending on the nature of the constituents or on other 25 factors.

It will be evident that many combinations of oxidizing and reducing agents are possible, the choice being dictated by considerations of thermal efficiency, the specific ferro-alloys involved, 30 economy, undesirable side reactions, and other factors.

It has been proposed, for example, by Udy in U. S. Patent No. 2,280,875 to introduce chromium into iron or steel by igniting in contact with the 35 iron or steel in the molten state an exothermic reaction mixture comprising high-carbon ferrochromium, silicon-containing material, and solid oxidizing material capable of reacting exothermically with carbon and silicon. In this 40 mixture the components are present in such amounts and proportions as to effect, upon ignition of the reaction mixture, oxidation and elimination of a portion of the carbon of the ferrochromium through reaction with the oxidizing 45

material in an amount sufficient to produce a substantial exothermic effect. Udy proposes as the oxidizing material an alkali metal nitrate, alkali metal chlorate, or alkali metal chromate.

In any exothermic addition agents of this type, exothermicity alone is not enough to assure the effectiveness of the agent. In order to be satisfactory for the addition of ferro-alloys to steel, such agents must not only generate at least a part of their own heat of solution but must dissolve readily in the molten metal. Unless rapid solution occurs, poor recovery of the ferro-alloy addition and bad segregation of the alloy in the steel result. It will be evident, therefore, that exothermicity and high rate of solution are complementary, and that one of the most important criteria for judging the effectiveness of these exothermic mixtures is rate of solution.

Potassium perchlorate is a powerful oxidizing agent, and by thermodynamics it can be shown that the oxidation of silicon by potassium perchlorate is potentially very strongly exothermic. Practically, however, under the conditions prevailing for the addition of ferro-alloys to steel, the reaction is difficult to initiate and propagate. This has been demonstrated by tests wherein pelleted mixtures of 100 mesh (0.0059 inch openings) 75% ferrosilicon and potassium perchlorate in stoichiometric proportions were added to molten seel in an induction furnace. The pellets merely floated on the surface of the steel with no visible signs of reaction and dissolved in the steel only very slowly if at all.

It is an object of the present invention to provide a mixture wherein potassium perchlorate and silicon may be reacted to provide exothermicity for introducing alloying elements into molten iron and steel.

Another object is to provide a mixture which will greatly increase the rate of solution of alloying materials in molten iron or steel.

Still another object is to provide such a mixture wherein carbon is essentially unoxidized in the reaction and, if present, may be introduced as an alloying element into the molten iron or steel.

A still further object is to provide a method of heating molten iron or steel by the use of the reaction mixture of the invention so as to facilitate 5 the addition of alloying elements to such metals.

The present invention is based upon the discovery that by the addition of an accelerator which promotes the reaction between silicon and potassium perchlorate, such as sodium carbonate 10 conveniently available as soda ash, to the potentially strong but otherwise difficultly reactable reaction mixture of silicon and potassium perchlorate, a controlled chemical reaction evolving considerable heat is produced. When the 15 reaction is applied by adding a mixture, suitably in pellets, of silicon, potassium perchlorate, and soda ash to molten iron and steel, for example, heat is transferred to the molten metal permitting the addition of alloying elements without 20 detrimentally chilling the metal. When the reaction is applied to ferro-alloys by incorporating the silicon, potasium perchlorate, and soda ash in mixtures of ferro-alloys, either pelleted or unpelleted, the solution of the alloys in molten 25 iron and steel is greatly improved.

When potassium perchlorate and silicon are pelleted with finely comminuted ferro-alloys such as ferrochromium, they are not especially helpful and, in fact, may retard solution of the alloy 30 in steel. Moreover, although potassium perchlorate will readily react exothermically with carbon or ferro-alloys containing carbon, as for example high-carbon ferrochrome, this exothermic reaction does not measurably improve the 35 rate of solution of the ferro-alloy in steel. When, however, a combination of silicon, potassium perchlorate, and an accelerator such as soda ash is employed as the active ingredient, the result is not only a high degree of exothermicity, as will be shown later in this specification, but an outstanding improvement in the rate of solution of the ferro-alloy. These effects are illustrated by the results of rate-of-solution tests listed in

Table I. The test procedure for making the rate-of-solution tests was as follows: A 100-lb. heat of steel was melted in an induction furnace and brought to a temperature of approximately 1600° C. A pelleted mixture of a measured quantity of ferroalloy, in this case 100 grams of chromium as highcarbon ferrochrome, and the active ingredients as specified, was added to the surface of the molten metal. The time necessary for the disappearance of the last vestiges of the addition was measured by stop watch and is considered to be an index of the solubility rate of the pellet. In Table I, the effect of even a small amount of soda ash is notable. The pellets employed for these tests and subsequent tests described in this specification were made by mixing the metallic constituents, 100 mesh by down in particle size, with potassium perchlorate and soda ash. No special sizing of the potassium perchlorate and soda ash was employed, these agents being used 65 in the fairly finely divided form normally available commercially. Mixing was accomplished by briefly shaking the constituents together after which water was added to the mixture until the particles would stick together. The mixture was 70 then compressed into cylindrical pellets  $1\frac{1}{2}$ inches in diameter and  $1\frac{1}{2}$  to  $2\frac{1}{2}$  inches long, on a hydraulic press at approximately 4000 p. s. i. The pellets were then dried in an oven at 150-200° C.

Effect of accelerator on rate of solution

	Comp	osition of H	Pellets, Per	cent	41-	
	High- carbon Ferro- chrome	Ferro- chrome Silicon	75% Ferro- silicon	Potas- sium Per- chlorate	Accele- rator (Soda Ash)	Time to Dissolve, Seconds
)	100 95 92. 5 90 90	  5		5 7. 5 10 5		60 54 65 61 75
5	89 88 87 86 85	5 5 5 5		5 5 5 5 5	1 2 3 4 5	32 36 36 31 33

In order that the mechanism of the invention may be more fully understood tests have been made which demonstrate (1) that an accelerator such as soda ash is essential for obtaining an effective reaction between silicon contained in the constitutents of the mix and potassium perchlorate for both high- and low-silicon alloys; (2) that with the accelerator present in accordance with the invention, silicon is oxidized in preference to carbon, so that when sufficient silicon is present to react with the potassium perchlorate, the carbon is unaffected and remains available for solution in the steel; and (3) that when carbon is present in the absence of an accelerator, carbon is oxidized as taught in the prior art by Udy even if silicon be present in an amount sufficient for reaction with all of the potassium perchlorate.

In these tests pelleted mixtures of ferro-chromium (high- and low-carbon), low-carbon ferrochromium-silicon, potassium perchlorate, and soda ash were prepared in which the pellets had the composition shown in Table II.

TABLE II

			Percent		·
Pellet	Carbon	Silicon	Chromi- um	Potassi- um per- chlorate	Soda ash
AB	4. 79 14. 74	41.9 39.5 5.06 5.60 5.57 5.69	31. 2 29. 4 62. 2 60. 3 59. 3 60. 5	15. 0 15. 0 5. 0 5. 0 5. 0	5. 0 2. 0 2. 0

<sup>1</sup> Includes carbon in soda ash.

Pellets A and B were tested by the solubility test procedure previously described in this specification with the results indicated below in Table III.

TABLE III

			<u> </u>
5		Pellet	Time to dissolve
	A (containing	g no accelerator)	Did not dissolve at all in 5 minutes.
	B (containing	g 5% soda ash as accelerator).	

The effect of the accelerator in pellet B in promoting the reaction and solution in steel of these high-silicon pellets is manifest. Without the accelerator, as shown by pellet A, the mixture was non-reactive and did not dissolve at all.

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Pellets C, D, E, and F were subjected to exothermicity tests. These tests were made by operating a 100-pound capacity induction furnace as a calorimeter. A heat of steel was melted down, thoroughly de-oxidized with manganese, 5 silicon and aluminum, and raised to a temperature of 1600° C. The power input to the furnace was then adjusted so that it was just sufficient to maintain the molten metal at constant temperature. When it was certain that constant tem- 10 perature was being maintained; i. e., when the heat showed no measurable temperature variation for a period of at least 5 minutes, a quantity of the specified pelleted mixture sufficient to add 1% chrominum to the steel was added. The 15 temperature of the heat was then observed until it again became constant at a new level. Temperatures were measured by means of a platinum vs. platinum plus 10% rhodium thermocouple encased in a refractory sheath continuously im- 20 mersed in the steel bath. The difference between the constant temperatures at the beginning and end of the test was considered to be a measure of the exothermic character of the pellets. The results of the tests are reliable comparisons of the 25 relative chilling effects of the various addition agents on molten steel. Samples of the steel were taken from the test heats immediately before and immediately after the pellet additions, and analyzed so that the relative oxidation and 30 recovery of carbon and silicon could be determined. The results of these tests are shown in Table IV.

The exothermic action of the potassium perchlorate-silicon-soda ash mixture in reducing the heat loss accompanying the addition of a ferro-alloy such as ferrochromium to molten steel is illustrated by Table V. Table V contains the results of measurements of the temperature change produced in 100-lb. heats of steel by the introduction of 1% chromium in the form of the various pelleted mixtures. These tests were conducted in the same manner as the tests shown in Table IV.

TABLE V

	Con				
	High-carbon Ferrochro- mium	Ferrocbrome Silicon	Potassium Perchlorate	Soda Ash	Temperature Drop of Steel in ° C.
	100 95 88 83	5 10	5 5 5 5	2 2 2	29 14 8 9
	78 83 83 40 34	10 5 5 60 51	10 10 7 7. 5	2 2 5 7. 5	1 4 6 22 7

The silicon in the mixture of the invention which contains an element to be alloyed with iron or steel must be at least sufficient to combine with all of the oxygen in the potassium perchlorate. An excess of oxygen will result in

TABLE IV

				Co	mposition (	of Steel, Pe	ercent	
Pellet	Temp. Drop of Steel in deg. C.	Solubil- ity, Time in Sec.	Ele- ment	Before Peliet Addition	After Pellet Addition	Change	Actually Intro- duced by Pellet	Recovery
C—Containing no accel- erator	17	76	{ C Si Cr	0. 015 0. 240 0. 01	0. 085 0. 264 0. 97	0. 070 0. 024 0. 96	0. 077 0. 081 0. 99	90. 9 29. 7 97. 0
D—Containing 2% soda ash	9	34	{ C Si Cr	0. 014 0. 133 0. 01	0. 090 0. 148 0. 96	0. 076 0. 015 0. 95	0. 976 0. 090 0. 97	100. 0 16. 7 98. 0
E—Containing 2% soda ash  T—Containing no accel-	11	33	C Si Cr C	0. 012 0. 110 0. 02 0. 011	0. 012 0. 120 0. 99 0. 011	0. 010 0. 97	0 094 0.99	10. 6 98. 0
erator	17	75	{ Si Cr	0. 232 0. 02	0. 260 0. 98	0. 028 0. 96	0. 092 0. 98	30. 4 98. 0

The pronounced effect of the accelerator in considerably increasing the exothermic power and greatly improving the solubility of the pellets in steel whether the mixtures contained carbon or not is clearly illustrated. The analytical 60 results show that in the case of the high-carbon pellets, C and D, all of the carbon was recovered from pellet D, which contained soda ash, but that carbon recovery from pellet C was incomplete. Moreover, silicon recovery from pellet C was much 65 greater than that from pellet D. These observations demonstrate that in the absence of the accelerator, a portion of the carbon in the pellet is oxidized as taught in the prior art, but that with the accelerator present, silicon alone is 70 oxidized while the carbon remains unaffected. The increased oxidation of silicon in pellets containing no carbon but in the presence of an accelerator is shown by a comparison of the tests on pellets E and F.

the oxidation of carbon and the alloying element in the mixture. The proportion of silicon in the grade of ferrochrome-silicon (50% silicon) used in the examples cited was slightly more than the stoichiometric equivalent of potassium perchlorate. Little additional improvement in exothermicity was observed when the ratio of ferrochrome-silicon to potassium perchlorate was increased beyond 1 to 1. The form to which the silicon is present, i. e., whether the silicon is a minor component of the ferro-alloy or is deliberately added as a silicon-rich alloy such as in the above cases, is unimportant as may be seen in Table VI below.

70 It may also be noted in Table V that potassium perchlorate alone reduced the temperature drop produced in molten steel by the addition of high-carbon ferrochrome. This is an illustration of the effect of the reaction of the oxidizing agent with the carbon of the ferrochrome according

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to the mechanism described in the prior art by Udy for some of his processes. However, it is of no importance in the present invention in view of the much greater effectiveness of the controlled silicon-potassium perchlorate-soda ash reaction. The present invention is just as effective with low-carbon ferro-alloys as shown in Table VI.

celerator is present in an amount sufficient to promote the reaction; the quantities of silicon, potassium perchlorate and accelerator being so proportioned to the alloying elements that upon ignition of the mixture in a bath of molten metal sufficient heat is generated to counteract the normal chilling tendencies of the alloying ele-

TABLE VI

C	Composition of P	ellets, Pero	cent			Tomner
Silicon-bear- ing Low- carbon Ferrochrome 1	Silicon-bear- ing Low- carbon Ferrochrome <sup>2</sup>	Low-car- bon Ferro- chrome	Potas- sium Per- chlorate	Soda Ash	Time of Solution, Seconds	Temper- ature Change, °C.
80	80	100	10 10	10 10	70 45 23	-20 + 1

<sup>Silicon-bearing low-carbon ferrochrome containing approximately 5% silicon.
Silicon-bearing low-carbon ferrochrome containing approximately 9% silicon.</sup> 

The data of Table VI were obtained from the results of exothermicity tests made as described previously.

Pellets of the last composition listed in Table VI were also used successfully to add 6% chromium to steel. A 50-lb. heat of low-carbon steel was melted in an induction furnace. The temperature of the heat was raised to 1650° C., and the power was turned off the furnace. The pellets were added to the steel with the power off. They dissolved in 25 seconds. The heat was held for a minute and a half with the power off and then poured into an ingot mold. It was still quite hot when poured, although a similar amount of plain ferrochromium added in that manner is known to chill the steel below pouring temperature before the addition is completely dissolved. 40 Chromium recovery was 90%, and there was no significant segregation within the ingot.

The potassium perchlorate-silicon-soda ash mixture is also effective in improving the solution of ferro-alloys in cast iron where the relatively low temperatures normally prevailing make solution of alloys such as ferrochrome somewhat difficult. Rate-of-solution tests similar to those described above in connection with Table I gave the results listed in Table VII for cast iron. The 50 temperature of the molten cast iron bath was approximately 1375° C. at the time of the addition.

ments contained therein and to increase the rate of solubility of said alloying elements.

Accordingly, the mixture may contain between 1% and 15% potassium perchlorate, at least 0.5% silicon, the atomic ratio of silicon to the oxygen of the potassium perchlorate being at least 0.5, and the accelerator being present in an amount sufficient to promote the reaction but not less than 0.5%, the remainder being alloying elements.

In a preferred embodiment of the invention, the mixture may contain between 3% and 10% potassium perchlorate, at least 1.2% silicon, the atomic ratio of silicon to the oxygen in the potassium perchlorate being at least 0.5; between 1% and 5% soda ash, the remainder being alloying elements.

The data in Table VIII, shows the effect of adding ferro-alloys and pellets containing silicon, potassium perchlorate, and soda ash to molten steel. In this application of the invention the mixture, suitably in the form of pellets, adds nothing to the molten steel except heat and perhaps some iron if the silicon is present in the form of ferro-silicon. The use of the exothermic pellet in this manner is particularly advantageous when the production of an exothermic alloy similar to the exothermic chrome alloy of the invention may not be justified on economic

TABLE VII

	Composition	of Pellets, Per	$\operatorname{cent}$		
High carbon Ferrochrome	Silicon-be ring Low-c: rbon Ferrochrome (9% Si)	Ferrochrome- Silicon	Potassium Perchlorate	Soda Ash	Time of Solution, Seconds
79	80	6	7. 5 10	7. 5 10	48 20

According to one aspect of the invention, the exothermic mixture comprises essentially alloying elements, silicon, potassium perchlorate and an accelerator such as soda ash; the components of the mixture being present in such quantities and being so proportioned that the silicon content is at least sufficient to combine with all of the oxygen in the potassium perchlorate, and the ac- 75 grounds. For present for an able for making the present in such quantities alloy can be obtained as a least sufficient to combine with all of the ac- 75 and soda ash.

grounds. For example, there is a limited use at present for an exothermic manganese alloy suitable for making ladle additions of manganese. But the net effect of an exothermic manganese alloy can be obtained by adding to a ladle ferromanganese and exothermic pellets of the invention containing silicon, potassium perchlorate, and sode ash

In Table VIII the data is based on the addition of 1% of an alloying element in the form of a ferro-alloy. The additions were made under conditions similar to those and in a furnace of the type described above.

#### TABLE VIII

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Composition of Pellets	Alloy Addition	Ratio of Potassium Perchlorate to alloy addition, grams/lb.	Reac- tion Time, Seconds	Temp. Drop,	1
56% Potassium perchlo- rate 34% Ferrosilicon (75% silicon) 10% Soda Ash	Chromium	25	50	19	1
57% Potassium perchlorate. 34% Ferrosilicon (50% silicon). 9% Soda Ash. 50% Potassium perchlo-	}do	87	40	10	2
rate. 45% Ferrosilicon (50% silicon). 5% Soda Ash	}do	45	71	16	
52% Potassium perchlorate. 43% Ferrosilicon (50% silicon). 5% Soda Ash	Manga- nese.	76	45	8	2
54% Potassium perchlo- rate. 44% Ferrosilicon (50% silicon). 2% Soda Ash	}do	80	43	8	3
	. :	i	1		

With an exothermic chromium-containing pellet, a ratio of 25 grams of potassium perchlorate per pound of chromium is adequate to permit the addition of one per cent chromium to molten steel with a temperature drop of about 10° C. It can be seen from Table VIII that a larger amount of potassium perchlorate is required to effect the same addition of chromium with a comparable heat loss when the exothermic pellet does not contain the chromium.

The exothermic mixture to be used principally for the addition of heat to molten iron and steel should have a minimum soda ash content of 2% 45 of the combined weights of the silicon and potassium perchlorate in the pellet. Smaller quantities of soda ash result in an unsatisfactory reaction rate or in no reaction at all. If too much soda ash is present in the pellet, there is a pos- 50 sibility that the mixture might be ignited prematurely, for example, by sparks. In general, no more than five per cent soda ash will be required. The silicon and potassium perchlorate should be present in sufficient quantities to insure a useful 55 exothermic reaction. In general, the mixture should have a minimum silicon content of 15%. Potassium perchlorate should be present in such quantities as to insure the presence of enough oxygen to react with the silicon if contamination 60 of the iron or steel with silicon is to be avoided. An excess of oxygen, if present, is not as undesirable as in the case of the pellet containing an alloying element since the excess oxygen has little or no harmful effects except possibly the 65 oxidation of small quantities of carbon and iron.

In the mixture of the invention which does not have incorporated therein an element to be alloyed with iron or steel, best results have been obtained with the following proportions of mate- 70 rials: 30% to 60% ferrosilicon containing at least 15% silicon, 70% to 40% potassium perchlorate, and at least 2% soda ash.

A preferred exothermic mixture according to the invention has the following composition: 54% 75

potassium perchlorate, 44% ferrosilicon (containing 50% silicon), and 2% soda ash.

The silicon in the above compositions, including those with as well as those without an alloying element, may be present in any of a number of forms. For example, it may be present as elemental silicon or as ferrosilicon. If alloying elements are present in the composition, silicon may be present as an alloy of silicon with the other alloying elements.

The method of the invention broadly comprises incorporating alloying elements in iron or steel by igniting in contact with molten iron or steel an exothermic mixture consisting essentially of silicon, potassium perchlorate and soda ash; the components of the mixture being present in such quantities and being so proportioned that the silicon content is at least sufficient to combine with all of the oxygen in the potassium perchlorate, and the soda ash is present in an amount sufficient to promote the reaction.

It is not necessary that the agents of the invention be pelleted or briquetted. Loose, unbonded mixtures are also effective. In general, however, pelleting or briquetting is preferred both for ease in handling and because, as is well known to the art, compacting such mixtures improves their efficiency by reason of closer contact of the active constituents. In this respect, the agents of this invention have a particular advantage because they require no special bonding agent or critical drying treatment.

The particle size of the comminuted constituents in these agents is not especially critical. It is a fundamental principle of chemistry, however, that the finer the particle size of the materials in a reactive mixture, the greater the ease with which those materials react, because of the increased contact area between the reactants. Moreover, it is old in the art that fine particle size facilitates pelleting. For the agents described above, a particle size to pass through a 100 mesh screen for the metallic constituents has been found convenient.

For certain types of prior art exothermic agents, particularly where reaction between carbon and the oxidizing agent occurs, a high degree of mixing or special blending, so that each particle of the metallic constituents is in contact with the oxidizing agent, is said to be necessary. For example, Udy teaches in relation to many of his prior art mixtures the use of an oxidizing agent of the group typified by sodium nitrate with a reducing agent such as carbon or silicon which may or may not be a part of the ferro-alloy, the whole essentially being bonded by raising the temperature of the briquetted mass to the fusion point of the oxidizing agent and cooling with the result that the particles of the briquet are cemented together by the oxidizing agent.

The agents of the present invention are sufficiently reactive and powerful that such special techniques are entirely unnecessary. With these agents it is only necessary to avoid major segregation of the reactants. This feature leads to more certainty of reaction and enables substantial economies in large-scale production of the agents.

The agents of this invention have many other advantages in addition to those already mentioned. For example, the silicon-potassium perchlorate reaction, when controlled as described by soda ash, is so effective that only a small amount of the reaction mixture need be added

to a ferro-alloy in order to gain great improvement in solution of the ferro-alloy. This is a definite economic advantage on the basis of production, handling, and transportation costs per unit of ferro-alloy. Furthermore, potassium perchlorate gives up no elements that may produce undesirable contamination in steel as do other oxidizing agents such as nitrates, permanganates, chromates, and manganese dioxide. Nitrates give off nitrogen which is harmful in many steels and may be particularly undesirable in nitrogensensitive steels such as the high-chromium steels. Other common oxidizing agents give up such elements as manganese and chromium that may not be desirable in certain instances. All of the 15 reaction products of the mixture of the invention escape from the steel. Moreover, potassium perchlorate gives off no noxious fumes as, for example, does sodium nitrate which gives off oxides of nitrogen. Analyses of the atmosphere over the heats in some of the tests described above have indicated the complete absence of measurable quantities of any noxious gases. The end products of the agent of the invention are a small amount of an innocuous silicate slag and potassium chloride which leaves the metal as a harmless vapor. In addition, it is known to chemical science that potassium perchlorate, although highly reactive, is more stable than the chlorates and, therefore, is less hazardous in handling and shipping.

Although various types of ferrochromium and ferromanganese were the ferro-alloys used in the examples of this invention described in this specification, the invention is not limited to these 35 materials. It is equally effective with any ferro-alloy, such as ferrovanadium, or any alloying element such as nickel or copper that is relatively inert and dissolves in steel or iron with the absorption of heat.

This application is in part a continuation of my copending application Serial No. 134,359, filed December 21, 1949, now abandoned.

What is claimed is:

1. An exothermic mixture consisting of sili- 45 con, potassium perchlorate, and soda ash, said silicon being present in an amount equal to at least 15% of said mixture, the proportions of silicon and potassium perchlorate in said mixture being such that the atomic ratio of silicon to the 50 oxygen in the potassium perchlorate is at least 0.5, said soda ash being present in an amount

equal to at least 2% of the combined weights of silicon and potassium perchlorate the remainder being substantially all iron and incidental impurities.

2. An exothermic mixture consisting of ferrosilicon, potassium perchlorate, and soda ash, said ferrosilicon having a silicon content such that at least 15% of said mixture is silicon, the proportions of silicon and potassium perchlorate in said mixture being such that the atomic ratio of silicon to the oxygen in the potassium perchlorate is at least 0.5, said soda ash being present in an amount equal to at least 2% of the mixture the remainder being incidental impurities.

3. An exothermic mixture consisting of 30% to 60% of ferrosilicon having a silicon content such that at least 15% of the mixture is silicon, 70% to 40% of potassium perchlorate, and at least 2% soda ash the remainder being incidental impurities.

4. An exothermic mixture consisting essentially of 1.5% to 15% potassium perchlorate, silicon being present in an amount of at least 0.5% and in such greater amount as is required to provide an atomic ratio of silicon to the oxygen in the potassium perchlorate of at least 0.5, soda ash in an amount between 0.5% and 10%, the remainder being alloying elements.

5. An exothermic mixture as claimed in claim 4 wherein chromium is a component of the alloying elements.

6. An exothermic mixture consisting essentially of 3% to 10% potassium perchlorate, silicon being present in an amount of at least 1.2% and in such greater amount as is required to provide an atomic ratio of silicon to the oxygen in the potassium perchlorate of at least 0.5, between 1% and 5% soda ash, the remainder being alloying elements.

DONALD C. HILTY.

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