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METHOD OF AND COMPOSITION FOR PURIFYING METALS

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The present invention relates to the refining of metals, notably iron and steel, and it has particular relation to the treatment of such metals for purposes of reducing the sulphur content thereof.

One object of the invention is to provide a purifier that will form a slag that will absorb sulphur from iron or steel and which when introduced into the molten metal evolves carbon dioxide and other gases smoothly and evenly over a relatively long period of time, to produce unusually effective agitation of the molten metal and resultant thorough absorption of the sulphur.

A second object of the invention is to provide a purifier for molten metals which is effective to reduce the sulphur content of the metal to an exceptionally low figure.

These and other objects will be apparent from consideration of the following specification and the appended claims.

It is well known that sulphur, even in relatively small amounts, is objectionable in metals such as iron or steel, because it produces so-called "shortness" and results in impairment of the strength of the metal. For this reason it is desirable to reduce the sulphur content of metals to a minimum. In order to accomplish this result it has heretofore been customary to add to the metals, while in molten state, small amounts of such materials as sodium cyanid, sodium carbonate, lime, or mixtures of lime, with sodium carbonate. These materials when introduced into the molten metal tended to decompose to liberate such gases as carbon dioxide, which were effective in agitating the metal and promoting thorough contact with the purifying agent. The latter under certain conditions tended to absorb a portion of the sulphur and at the same time formed a relatively fluid slag which floated to the top of the molten metal where it could be removed. Pulverulent forms of the purifiers tended to decompose upon the surface of the metal and were in part disseminated by the gases as dust without effective contact, and therefore the amounts of sulphur removed thereby were relatively small. In order to overcome this defect it has been proposed to admix the purifier with a binder such as tar or molasses and then to form the mixture into briquettes of suitable size. These briquettes tended to retain their form for a short time even in molten metal and when they were used there was less loss of the purifier through rapid surface decomposition and through dissemination of the purifier as a dust by reason of the violent evolution of gases upon the surface.

However, even where the purifiers were briquetted with molasses or tar, the results were not entirely satisfactory because the binder quickly decomposed before sufficient time was afforded for thorough contact with the metal. By reason of the shortness of the life of the binder in the molten metal the masses soon disintegrated and the period of agitation of the metal was relatively short and violent. Furthermore, many of the purifying agents such as sodium carbonate tended to evolve only relatively small quantities of carbon dioxide and other gases, and therefore the thoroughness of the agitation of molten metal was further reduced. Moreover, molasses and tar are quite sticky and tend to adhere to molds used in briquetting.

The present invention is designed to overcome the foregoing objectionable features encountered in purifiers employed in the treatment of molten iron and steel by combining materials which are exceptionally rich in gas-forming constituents with a highly heat-resistant organic binder. Sodium bicarbonate constitutes an excellent example of a sodium compound which may be employed in practicing the invention. The resin-like residue formed in the pressure stills and other apparatus employed in the cracking and refining of mineral oils, in order to form motor fuels and lubricants, constitutes a suitable binder for use in connection with the sodium bicarbonate.

When such composition is formed into briquettes the binder does not stick to the molds. Moreover, when the briquettes are introduced into molten iron or steel the sodium bicarbonate decomposes to give off very large amounts of carbon dioxide. The still residues are relatively resistant to the high temperatures encountered in the bath, and therefore they maintain the integrity of the briquettes for considerable periods of time so that the heat does not penetrate into and decompose all of the sodium bicarbonate immediately. Accordingly, the copious evolution of carbon dioxide and other gases is prolonged over a considerable period of time and there is no extremely violent evolution of gases upon first contact of the purifier with the molten metal. The binder itself is gradually consumed to form carbon dioxide and water and these go to increase the total volume of gases produced. As a result of all of these phenomena there is thorough and relatively prolonged agitation of the metal with the purifier which results in higher, effective and complete purification of the metals from sulphur compounds. Excellent opportunity is also afforded for collection and flotation of any small particles of slag or other mechanically sus-

pended impurities which may be disseminated through the molten metal.

The composition of briquettes prepared in accordance with the present invention is susceptible of considerable variation. For example, the briquettes may consist almost entirely of a mixture of sodium bicarbonate with still residues. The amount of residue may be only sufficient to bind the sodium bicarbonate together as a coherent mass, but if desired the amount of residue may also be increased for purposes of introducing a larger percentage of reducing carbon in the molten metal. Various other constituents may be introduced into the composition. For example, a part of the sodium bicarbonate may be replaced by sodium carbonate. Certain features of the invention may even be realized where the sodium bicarbonate is entirely replaced by sodium carbonate. Calcium carbonate alone or in admixture with sodium carbonate may replace a portion of the sodium bicarbonate. In order to increase the amount of gases evolved from the material, water may be incorporated in order to produce steam upon contact of the purifier with the hot metal. Likewise, manganese dioxide and other agents which are found to promote purification may be incorporated in suitable proportions.

A specific example of a composition embodying the principles of the present invention comprises:

Sodium carbonate	88 parts
Sodium bicarbonate	10.4 parts
Water	1.4 parts
Still residues	20 gals. per ton of the above mixture

These are simply mixed together and briquetted.

For purposes of determining the value of this material in the removal of sulphur from iron a stock containing originally .083% of sulphur was treated in the molten state for a period of six minutes, with 0.45% of the foregoing composition in briquette or lump form. At the conclusion of the treatment analysis showed that the sulphur content of the iron had been reduced to .038%. In a second test conducted similarly upon iron containing originally .082% of sulphur .75% of purifier was employed. The sulphur content of the iron was reduced to .024%.

A second composition suitable for practicing the invention comprises a mixture consisting of sodium carbonate 76 parts, sodium bicarbonate 20.8 parts, water 2.8 parts, still residue in the ratio of 20 gallons per ton of mixture. This purifier in a ratio of 0.45% was added to a sample of molten iron containing originally .091% of sulphur. The sulphur content at the conclusion of the treatment was .036%.

For purposes of comparison tests were conducted with briquettes comprising a mixture of sodium carbonate and molasses in an amount sufficient to thoroughly bind the sodium carbonate as a purifier. In this test a sample of iron containing originally 0.072% of sulphur was treated for six minutes with 0.45% of the purifier. The sulphur content was found to have been reduced to 0.045%. In a further comparative test a sample of iron containing 0.072% of sulphur was treated with .5% of a commercially available purifier. The sulphur content was reduced to 0.053%.

In a test designed to show the effects of the use of sodium carbonate and still residues in the absence of sodium bicarbonate a composition consisting of 89 parts of sodium carbonate and 11 parts of water was mixed with pressure still residues in the ratio of 20 gallons per ton of the mixture. A sample of iron containing .075% of sulphur was then treated for six minutes with .62% of this composition. The sulphur content of the sample was reduced to .056%.

In the use of briquettes prepared in accordance with the provisions of the present invention the briquettes are thrown into the molten metal and may then be rabbled or pushed about by means of suitable poles, preferably of green wood. The purifier may be employed in substantially any of the conventional processes of refining or otherwise manipulating molten iron or steel. For example the briquettes may be placed in the bottom of the bull ladle and the molten metal allowed to pour down over them from the cupola, or other type of furnace. Purification may likewise be effected by adding the briquettes to the iron as it is poured from the blast furnace. In the latter process the purified iron may then be further treated in an open hearth furnace, Bessemer converter, or subjected to other conventional treatment. It is also possible to desulphurize the metal directly in the open hearth furnace (either acid or basic) or in a Bessemer converter. Such treatment may precede or follow the conventional blowing treatment in the furnaces. Preferably the slag upon the molten metal is removed prior to desulphurization. However, such removal is not in all cases required. In the case of steel the desulphurizing treatment may precede recarbonizing. Indeed, it is possible to employ the still residues constituting the binder in the desulphurizing material as all or a part of the source of carbon in the recarbonizing material in the recarbonizing process.

From the foregoing examples, it will be apparent that desulphurizing material containing sodium bicarbonate and still residues as components are substantially more effective in the desulphurization of iron or steel than conventional purifiers.

Although only the preferred forms of the invention have been described, it is to be understood that these are merely exemplary, and that numerous modifications may be made therein without departure from the spirit of the invention or the scope of the appended claims.

What I claim is:

1. A desulphurizer for metals consisting of briquettes containing sodium bicarbonate and still residues derived from the distillation of mineral oil.

2. A method of desulphurizing iron or steel which comprises adding to the molten metal a briquette comprising sodium bicarbonate admixed with pressure still residues derived from the distillation of mineral oil.

3. A composition for desulphurizing iron or steel consisting of sodium bicarbonate, sodium carbonate and still residues derived from the distillation of mineral oil.

4. A composition for. desulphurizing iron or steel consisting of sodium bicarbonate, sodium carbonate and water in a binder consisting of still residues derived from the distillation of mineral oil.

5. A method of desulphurizing molten iron or steel which comprises adding thereto briquettes consisting of a mixture of sodium carbonate, sodium bicarbonate, water and still residues derived from the distillation of mineral oil as a binder and removing the resultant slag.

6. A composition for desulphurizing iron or steel comprising a desulphurizing carbonate of

a metal in finely divided form admixed with still residues derived from the distillation of mineral oil.

7. A method of desulphurizing iron or steel which comprises adding to the metal in molten state mixture of finely divided desulphurizing carbonate of a metal and still residues derived from the distillation of mineral oil.

8. Composition of matter for purifying metals which melt at high temperatures comprising a material which in the molten metal is decomposed into a gas and molten residue of alkaline reaction, said material being admixed with a still residue derived from the distillation of mineral oil.

9. A composition of matter for use in purifying molten iron and steel, comprising a sodium carbonate admixed with a resin like residue from the pressure distillation of petroleum.

10. A composition as defined in claim 9 in which the carbonate is the bicarbonate.

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