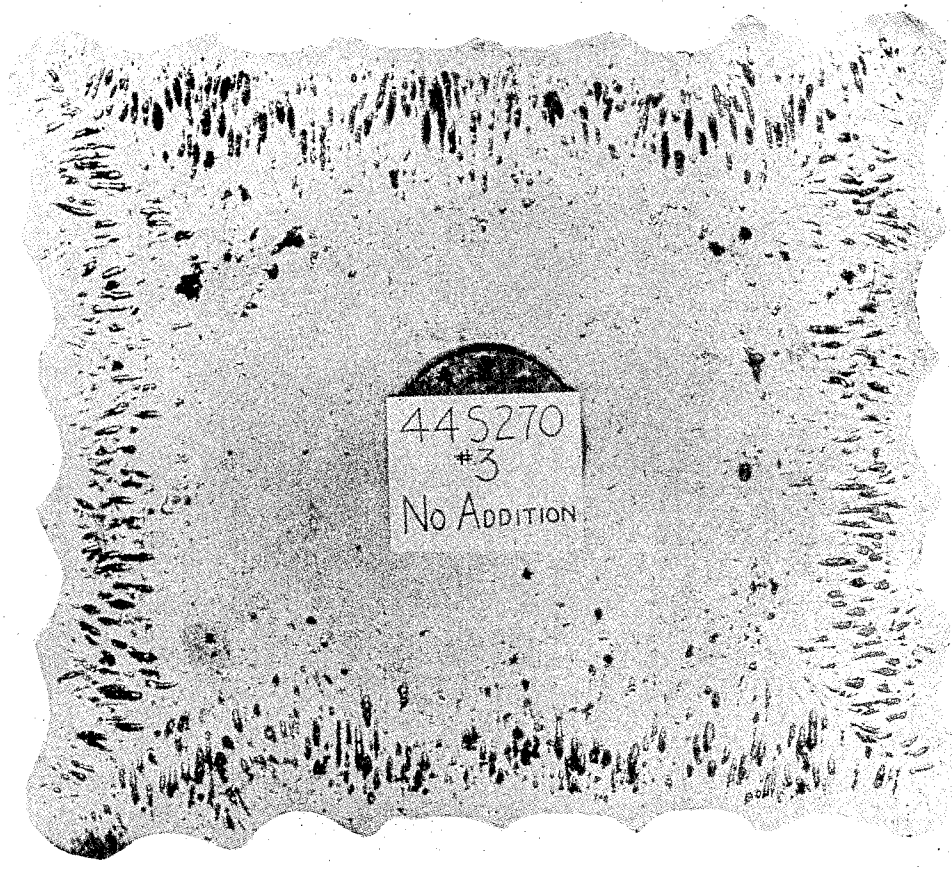
Nov. 28, 1939. S. EPSTEIN ET AL 2,181,693

STEEL TREATMENT

Filed Sept. 8, 1937 5 Sheets-Sheet 1

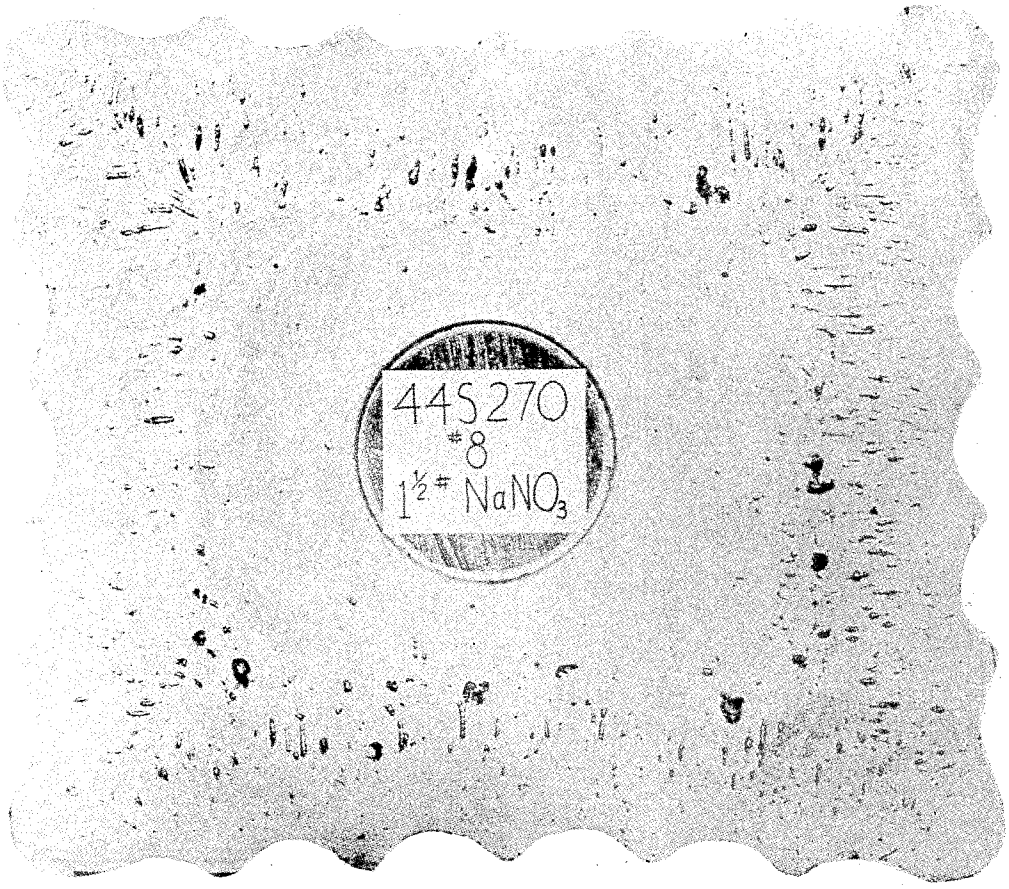
Fig. 1a.



Ingot No. 3. poured without any mold addition.

Inventors
Samuel Epstein
and *Hugo C. Larson.*
By *R. S. C. Dougherty.*
Attorney

Fig. 1b.



Ingot No. 8. treated with 1½ # $NaNO_3$.

Inventors
and Samuel Epstein
Hugo C. Larson.
By R. S. C. Dougherty.
Attorney

Nov. 28, 1939. S. EPSTEIN ET AL 2,181,693
STEEL TREATMENT
Filed Sept. 8, 1937 5 Sheets-Sheet 3

Fig. 2a.

Heat 44S270.

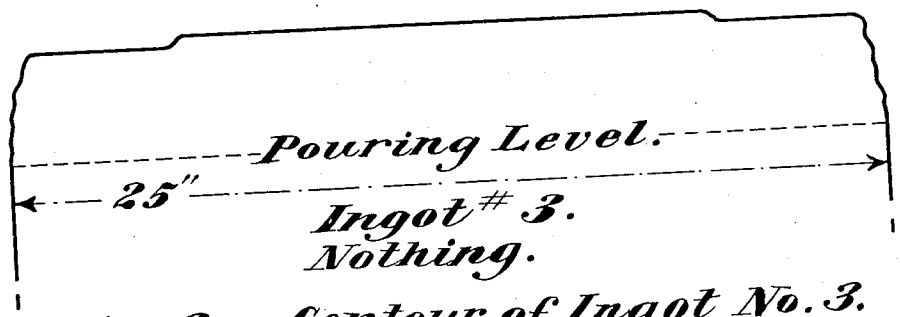


Fig. 2a. Contour of Ingot No. 3.

Fig. 2b.

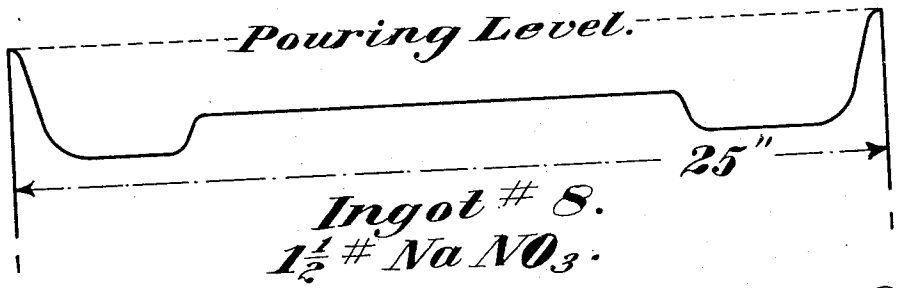
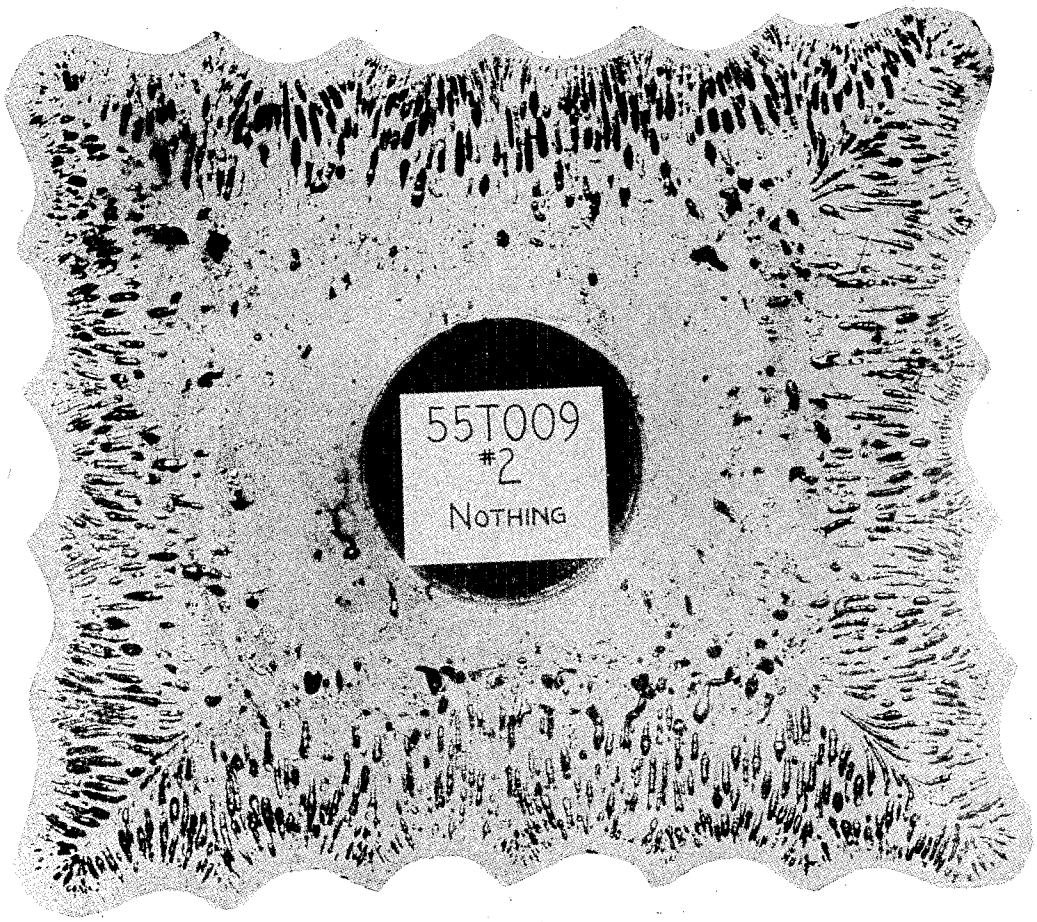


Fig. 2b. Contour of Ingot No. 8.

Inventors
Samuel Epstein
and Hugo C. Larson
By R. S. C. Dougherty. Attorney

Nov. 28, 1939. S. EPSTEIN ET AL 2,181,693
STEEL TREATMENT
Filed Sept. 8, 1937 5 Sheets-Sheet 4

Fig. 3a.



Ingot No. 2 poured without any mold addition.

Inventors
Samuel Epstein
and *Hugo C. Larson.*
By *R. S. C. Dougherty.*
Attorney

Nov. 28, 1939. S. EPSTEIN ET AL 2,181,693
STEEL TREATMENT
Filed Sept. 8, 1937 5 Sheets-Sheet 5

Fig. 3b.



Ingot No. 4 treated with 1# of a 3:3:4 $NaNO_3$ - $Na_2Cr_2O_7$ - Fe_2O_3 mix.

Inventors
and *Samuel Epstein*
Hugo C. Larson.
By *R. S. & C. Dougherty.*
Attorneys

Patented Nov. 28, 1939

2,181,693

UNITED STATES PATENT OFFICE

2,181,693

STEEL TREATMENT

Samuel Epstein, Bethlehem, and Hugo C. Larson, Johnstown, Pa., assignors to Bethlehem Steel Company, a corporation of Pennsylvania

Application September 8, 1937, Serial No. 162,848

12 Claims. (Cl. 75—56)

This invention relates to controlling the rimming action of steel so that the solidified ingot has a thick-skinned butt which will not crack and tear during rolling and hence give billets with good surface.

Rimming steel gives off large quantities of gases (Co, N_2, H_2, CO_2), mainly carbon monoxide, while it is poured into the ingot mold and during solidification. This gas evolution causes the ingot to have a spongy structure without any central shrinkage cavity or pipe. To eliminate pipe and undue sponginess and to get a tough-skinned ingot at the same time requires close control of the rimming action.

If the steel as poured contains too much reactive oxygen and thus tends to give off too much carbon monoxide it acts "wild" in the mold. On pouring, the mold fills up rapidly with the molten metal which contains large bubbles of the evolving gas. Then as the gas suddenly escapes the height of the metal in the mold sinks sharply and the mold requires further filling. Such an ingot may sink again before solidifying so that a pipe is formed (sheet or strip rolled from such steel may also have the defect called "lamination") or it may rise. In the latter case long pencil-like blowholes close to the surface of the ingot and perpendicular to it are formed at the lower portion or butt. The butt of such an ingot gives poor surface in rolling.

We have found by experience that if the steel as poured contains the proper amount of reactive oxygen to form the proper amount of CO, the metal fills the mold more steadily. After filling the metal holds its level and the surface quickly assumes an active boiling appearance. Soon the characteristic crust or rim begins to form from the sides inward, from which the term rimming steel is derived. The crust or solidified top of the ingot is either at the same level as that to which the molten steel was poured, or an inch or two lower. Such an ingot has no pipe and fewer of the long pencil-like blowholes appear at the butt so that it gives a better surface in rolling.

On the other hand, if the steel as poured contains too little reactive oxygen, too little CO is evolved. The metal fills the mold steadily and retains its level but the boiling action may be somewhat more sluggish. Then the ingot slowly begins to rise in the mold, the amount of rise varying from an inch or two to as much as eight or ten inches. Such an ingot has a thin-skinned butt with large pencil-like blowholes which cause poor surface in rolling.

To avoid a "wild" or strongly falling steel on the one hand and a rising steel on the other, a certain amount of deoxidizer has to be used in the ladle of low carbon steel in order to leave the right amount of active oxygen in the steel. The correct amount of deoxidizer can be judged from the composition of the bath and slag in the furnace. Usually appreciably less deoxidizer is added to the ladle than is likely to produce a rising steel in the mold. If a steel which falls sharply in the molds results, the falling tendency can be overcome by adding the proper amount of the deoxidizer aluminum in the succeeding molds. Fairly frequently, however, the correct deoxidizing ladle addition cannot be judged accurately and the steel rises in the mold. Rimming steel containing about 0.15 per cent carbon or higher invariably tends to rise in the mold even without the addition of any deoxidizer in the ladle. In these instances it is advantageous to add some substance to the ladle or mold which has an effect exactly the opposite of a deoxidizer and hence causes the steel to hold steady or fall slightly in the mold instead of rising.

The obvious explanation for the formation of the pencil-like blowholes at the butts is the entrapment of gases which are evolved during solidification. In the upper half of the ingot the gases can escape to the outer air more readily because of the smaller ferrostatic head of molten metal. At the lower half of the ingot or butt the greater ferrostatic head of the molten metal above can prevent escape unless the evolved gas has sufficient pressure to overcome the ferrostatic pressure. If as solidification takes place, the gases evolved at the lower part of the ingot are entrapped, the ingot naturally rises in the mold.

Evidently it is not enough for gases to be given off early in the pouring period. The gases must be evolved precisely during the time when solidification is proceeding so that the gases evolved at the surfaces of the solidifying crystals in the change from the liquid to the solid state, can be swept out and can exert enough pressure to escape.

We have found that a simple and effective way to produce such a gas evolution is to add a strong oxidizing substance to the steel, of the class of strong oxidizers like potassium chlorate, sodium nitrate, potassium permanganate, and potassium dichromate. Presumably the oxygen in the strong oxidizer immediately forms FeO on coming in contact with the molten steel. This FeO along with the FeO already present remains in

solution in the molten steel; but FeO is rejected by the solidified steel during solidification. As soon as the molten steel is enriched by this rejected FeO the latter reacts with the carbon in the molten steel according to the equation $FeO+C=CO+Fe$. Thus more CO is evolved at the surface of the solidifying crystals and this helps increase the gas pressure to above what it would be if the strong oxidizer were not added. The gases evolved can thus escape.

Of the strong oxidizers sodium nitrate is the cheapest. It was found, however, that on adding it to the molds of rimming steel during pouring a rather loud explosion would occasionally occur. The tendency to explode was completely eliminated by mixing the sodium nitrate with finely powdered Fe_2O_3. Our practice has been to fuse the sodium nitrate and add the powdered Fe_2O_3 stirring up the mixture and casting it into ½ lb. cakes. These cakes are very strong and are conveniently handled on the pouring platform. For example, the proportions may be 60 parts sodium nitrate to 40 parts Fe_2O_3 by weight. This has been satisfactory but a lesser or greater proportion of Fe_2O_3 may also be used. The sodium nitrate may run from 35% to 90% while the ferric oxide may run from 65% to 10%. The cast cakes of the oxidizing agent, of definite and moderate weight, are of considerable practical advantage in enabling the operator to add the necessary amount of the re-agent. It is obvious that the amount of re-agent necessary will vary with the different castings, and the same cakes of definite weight enable the operator to add the requisite amount in any particular instance. Cakes of the mxiture can also be made without fusing but by mixing dry, adding a suitable binder and molding under pressure in a die.

For low carbon rimming steel about 2 to 16 oz. per ton of the 60:40 $NaNO_3$—Fe_2O_3 mix are required depending upon the degree of deoxidation of the steel. This amount may be added in the ladle or mold, preferably the latter. For higher carbon rimming steel the amount of the mix required may be two to three times that for lower carbon steels. In using proper amounts of the mix not enough nitrogen is absorbed from the sodium nitrate to harm the steel in any way. The greatest benefit is conferred by adding the mix to a rising steel. However, our work indicates that even in the case of a falling steel the addition of the mix gives an ingot with a somewhat thicker and sounder skin at the butt.

Figs. 1*a* and 1*b* show photographs of cross-sections through the butts about 12 inches from the bottom of two 22" x 25" rimming steel ingots from the same heat. In A of ingot #3 no addition was made to the mold; in B of ingot #8, 1½ lbs. of sodium nitrate was added to the 4-ton ingot. Note the large pencil-like blowholes near the surface in the untreated ingot and the much smaller blowholes further removed from the surface in the treated ingot.

Figs. 2*a* and 2*b* show the contours of the tops of the same ingots. Ingot #3 with no mold addition rose about 3 inches, where as ingot #8 with an addition of 1½ lbs. of sodium nitrate fell about 3 inches.

Figs. 3*a* and 3*b* show photographs of cross sections similar to those of Figs. 1*a* and 1*b* of 2 ingots from another heat. Ingot #2 untreated has numerous large pencil-like blowholes near the surface. Ingot #4 treated with 1 lb. of a 3:3:4 sodium nitrate-sodium dichromate-Fe_2O_3 mix shows no pencil-like blowholes near the surface.

Table I shows the distinct improvement in surface produced by using the sodium nitrate-Fe_2O_3 mix as determined by careful inspection of billets rolled from ingots from 6 heats, ingots from 6 heats being treated with the mix and other ingots from the same heats not being treated. The defective areas were outlined and measured and the results expressed as sq. in. of defective area per sq. ft. of billet surface.

TABLE I.—*Summary of surface defects in billets cut from the butts of 60 ingots from 6 heats*

Mold addition	Defective areas—sq. in. per sq. ft.				
	No. of ingots	Seams	Scabs	Ingot cracks	Alligator hide
Nothing	20	1.88	1.8	.08	8.0
Sodium nitrate-Fe_2O_3 mix	40	1.3	1.3	.07	.47

Note that alligator hide which is the most serious defect was almost completely eliminated by the mix. The amount of seams and scabs was also materially reduced.

We appreciate the fact that various substances have previously been added to rimming steel for the purpose of controlling the rimming action. Sodium carbonate and calcium fluoride have been used or proposed for use. We have found, however, that the best results in this control can be obtained by using such substances as those mentioned above, namely strongly oxidizing substances. For characterizing the type of material which we have found to be most effective, they are such substances as are decomposed or dissociated to liberate oxygen at the temperature of molten steel, at the time of casting.

While we have referred to the use of Fe_2O_3 for preventing the explosive action sometimes accompanying the use of strongly oxidizing substances, we do not desire to limit ourselves to the use of the particular substance Fe_2O_3. Frequently its use is unnecessary. Furthermore, other diluents or interspersing agents may be employed. We prefer to use such a diluent or interspersing agent as an oxide which is not broken down at the temperature of the molten steel at the time of tapping or casting. Roll scale, for example, may be successfully used.

Having thus described our invention what we claim as new and desire to secure by Letters Patent is:

1. The method of manufacturing rimmed steel comprising the step of adding a highly oxidizing agent of the group comprising potassium chlorate, sodium nitrate, potassium permanganate and potassium dichromate and their equivalents to the molten metal after tapping.

2. The method of manufacturing rimmed steel comprising the step of adding sodium nitrate to the molten metal after tapping.

3. The method of manufacturing rimmed steel comprising the step of adding sodium nitrate and iron oxide together to the molten metal after tapping.

4. The method of controlling the rimming action of steel to obtain an ingot with a thick-skinned butt, comprising the addition to the molten rimming steel after tapping of an oxidizing substance of the group comprising potassium chlorate, sodium nitrate, potassium permanganate and potassium dichromate and their equivalents.

5. The method of controlling the rimming ac-

tion of steel to obtain an ingot with a thick-skinned butt, comprising the addition to the molten rimming steel after tapping of a mixture of an oxidizing substance of the group comprising potassium chlorate, sodium nitrate, potassium permanganate, potassium dichromate and their equivalents and a diluent of weaker oxidizing action than said oxidizing substance.

6. The method of controlling the rimming action of steel to obtain an ingot with a thick-skinned butt, comprising the addition to the molten rimming steel after tapping of a mixture of sodium nitrate and a diluent having a weaker oxidizing action than sodium nitrate.

7. The method of controlling the rimming action of steel to obtain an ingot with a "thick-skinned" butt, comprising the addition to the molten rimming steel after tapping of an oxygen containing substance of the group comprising potassium chlorate, sodium nitrate, potassium permanganate and potassium dichromate and their equivalents.

8. The method of controlling the rimming action of steel to obtain an ingot with a thick-skinned butt, comprising the addition to the molten rimming steel after tapping of sodium nitrate.

9. The method of controlling the rimming action of steel to obtain an ingot with a thick-skinned butt, comprising the addition to the molten rimming steel after tapping of a sodium nitrate-iron oxide mixture, the proportions of this mixture varying from about 10 per cent to 65 per cent iron oxide.

10. The method of controlling the rimming action of steel to obtain an ingot with a thick-skinned butt, comprising the addition to the molten rimming steel after tapping of a sodium nitrate-Fe_2O_3 mixture, the proportions of this mixture varying from about 10 per cent to 65 per cent Fe_2O_3.

11. The method of controlling the rimming action of steel to obtain an ingot with a thick-skinned butt, comprising the addition to the molten rimming steel while pouring in the mold of from 2 oz. to 48 oz. per ton of a sodium nitrate-iron oxide mixture.

12. The method of controlling the rimming action of steel to obtain an ingot with a thick-skinned butt, comprising the addition to the molten rimming steel in the ladle of from 2 oz. to 48 oz. per ton of a sodium nitrate-iron oxide mixture.

SAMUEL EPSTEIN.
HUGO C. LARSON.