

UNITED STATES PATENT OFFICE.

OSKAR NAGEL, OF HAMBORN, GERMANY.

PROCESS OF MAKING SPELTER.

SPECIFICATION forming part of Letters Patent No. 766,279, dated August 2, 1904.

Application filed January 12, 1903. Serial No. 138,732. (No specimens.)

To all whom it may concern:

Be it known that I, OSKAR NAGEL, a citizen of the United States, residing at Hamborn, Rheinland, Germany, have invented a certain new and useful Process of Making Spelter, of which the following is a specification.

My invention relates to an improved process for making spelter, designed especially to be carried out in a blast-furnace, with consequent economy in the cost of production; but the invention is not limited to the making of spelter in such an apparatus.

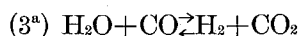
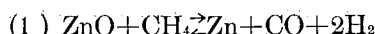
In my Patent No. 699,969, of May 13, 1902, I describe a process of producing spelter by reducing zinc oxid in a blast-furnace or similar apparatus by means of water-gas. In that patent I call attention to the fact that previous experiments were unsuccessful on account of the great quantity of combustion-gases and nitrogen in the zinc atmosphere which prevented the liquid condensation, but resulted only in the production of zinc-dust. As a result of further experimenting along the lines indicated by me in that patent I have found that hydrocarbons in gaseous or gasified condition, including, of course, coal-gas and natural gas, are equal and sometimes superior to water-gas for carrying the process into effect. Natural gas containing from eighty-five to ninety per cent. of methane (CH_4) is especially advantageous, as the concentration of zinc-vapors obtained is nearly twice as large as with water-gas. This superior result can be theoretically explained by the fact that one molecule of water-gas ($\text{CO} + \text{H}_2$) combines only with two atoms of oxygen, but one molecule of methane combines with four atoms of oxygen. Furthermore, the coefficient of molecular friction of methane is only about half of that of water-gas, which fact explains the easy condensation of zinc in a methane atmosphere. On account of these superior qualities of methane as compared to water-gas for the purpose a considerable quantity of nitrogen may become added to methane without affecting the reducing capacity of the latter as compared to water-gas. I find, for instance,

that a mixture of ninety per cent. methane and ten per cent. nitrogen is superior to water-gas and that a mixture of eighty-five per cent. methane and fifteen per cent. nitrogen is about equal to water-gas. A further increase of nitrogen in the natural gas makes it of course inferior to water-gas. As natural gas with eighty-five to ninety per cent. methane and two to fifteen per cent. of nitrogen occurs very frequently, (containing sometimes 0.20 per cent. sulfureted hydrogen, which, however, is not injurious at the heat of the zinc reduction,) I am enabled to always utilize a cheap substitute for the water-gas and which, in fact, as I have indicated, is often very superior to the latter. Besides methane, natural gas, or coal-gas any other gaseous or gasified hydrocarbons or mixtures of these with water-gas can be used for my purpose, as in the heat they act alike. The atmosphere of all these hydrocarbons in gaseous or gasified form is eminently reducing and allows of an easy condensation to liquid metal.

In the use of the process with a gaseous or gasified hydrocarbon, as indicated, I proceed in practically the same way as I have described in my said patent in connection with water-gas. By passing such heated hydrocarbons through a zinc ore or a mixture of ore with from ten to fifteen per cent. of coal the zinc oxid is reduced, the hydrocarbon being split up into carbon monoxid and hydrogen, analogous to the splitting up of hydrocarbons by superheated steam. Methane gives in this reaction one molecule of carbon monoxid and four atoms of hydrogen, (CH_4) and ethane in the same reaction gives two molecules of carbon monoxid and six atoms of hydrogen, (C_2H_6).

The difference between the present process and the one described in my previous patent is that with the patented process the water-gas—i. e., carbon monoxid and hydrogen—is the only reducing agent, whereas with the present process the hydrocarbons perform a reducing action partly by being split up into carbon monoxid and hydrogen and partly by these two substances formed by their destruc-

tion. We have, therefore, the following reactions:



Equation No. 1 shows the splitting up of the hydrocarbon and is readily understood. In equation No. 2 the reduction is continued and the equation with increasing temperature is going to the right, since the reaction is absorbing heat to the right side. The reaction is easy, owing to the great difference in the heat formation—*i. e.*, ($\text{ZnO} =$) eighty-five thousand calories minus ($\text{H}_2\text{O} =$) fifty-eight thousand calories equal twenty-seven thousand calories. The water formed in equation No. 2 is partly reduced by methane, which is understood from equation No. 3^b and partly by the equation No. 3^a. The equation No. 3^a is going entirely to the right side until the concentration of CO_2 becomes so great as to correspond to the equilibrium at this temperature. The calculation shows that for each given temperature in the equilibrium the proportion of the partial pressures must be constant, as will be understood by persons familiar with chemical dynamics. The reaction indicated by equation No. 2 gives, therefore, $\frac{\text{CH}_2\text{O}}{\text{CH}_4} = K$, while the reaction indicated in equation No. 3^a gives $\frac{\text{CH}_3\text{CCO}_2}{\text{CCOCH}_2\text{O}} = K'$, (C meaning concentration.) Therefore $\frac{\text{CCO}_2}{\text{CCO}} = K'K = K''$. As with increasing temperature K is increasing, so K'' must also increase, meaning, therefore, an increasing effect in the yield. The result of these reactions is an atmosphere practically free of oxygen, oxidizing substances, and nitrogen, thus allowing for an easy concentration of the zinc-vapors to liquid metal.

It is advantageous, but not necessary, to mix about fifteen per cent. of coal to the ore, as thereby the reactions are helped and their velocity increased.

Generally speaking, the same reactions take place if instead of using methane or natural gas any other gaseous or gasified hydrocarbon or mixture of hydrocarbons is used.

By this process any natural or roasted material containing zinc oxid, zinc carbonate, zinc silicate, or zinc hydrate, or mixtures of the same can be reduced—such, for example, as roasted blende of any grade, roasted galena-blende, franklinite, willemite, zincite, calamin, smithsonite, hydrozincite, &c.

My present process is carried into effect in the same way as my water-gas process described in my patent before referred to. The hydrocarbons are heated in ovens or recuperators and injected into the furnace or reducing-chamber containing the charge. The cooled zinc-vapors are condensed in a suitable apparatus for the purpose.

It will be understood, of course, that my process can be carried out in connection with the condensation of zinc-vapors obtained by any other process or reaction—as, for example, by heating blende with iron or iron silicate. It will also be understood that zinc-vapors prepared in a blast-furnace, as I have described, can, if desired, be oxidized by a current of air to produce pure oxid of zinc instead of being condensed to spelter in a condensation apparatus.

Having now described my invention, what I claim as new, and desire to secure by Letters Patent, is as follows:

1. An improved process for reducing zinc oxidic ores, which consists in subjecting the material to the reducing effect of hydrocarbons in gaseous or gasified form heated previously to entrance in the reducing-chamber, substantially as set forth.

2. An improved process for making spelter from zinc oxidic ores, which consists in subjecting the material to the reducing effect of gaseous or gasified hydrocarbons heated previously to entrance in the reducing-chamber, and in cooling the resulting zinc-vapors in an atmosphere of such gas, substantially as and for the purposes set forth.

3. An improved process for making spelter from zinc oxidic ores or zincic materials, which consists in subjecting a mixture of such material and coal to the reducing effect of gaseous or gasified hydrocarbons heated previously to entrance in the reducing-chamber, and in cooling the resulting zinc-vapors in an atmosphere of such gas, substantially as and for the purposes set forth.

4. An improved process for reducing zinc oxidic ores, which consists in subjecting the material to the reducing effect of natural gas, the said gas being highly heated previous to entrance in the reducing-chamber, substantially as and for the purposes set forth.

5. An improved process for reducing zinc oxidic ores, which consists in subjecting the material to the reducing effect of natural gas, the said gas being highly heated previous to entrance in the reducing-chamber, and in cooling the resulting zinc-vapors in an atmosphere of such gas, substantially as and for the purposes set forth.

6. An improved process for reducing zinc oxidic ores, which consists in subjecting the material to the reducing effect of a gas composed almost entirely of methane, the said gas

being highly heated previous to entrance in the reducing-chamber, substantially as and for the purposes set forth.

7. An improved process for reducing zinc
5 oxidic ores, which consists in subjecting the material to the reducing effect of a gas composed almost entirely of methane, the said gas being highly heated previous to entrance in the reducing-chamber, and in cooling the
10 resulting zinc-vapors in an atmosphere of such gas, substantially as and for the purposes set forth.

8. An improved process for reducing zinc
15 oxidic ores, which consists in subjecting the material to the reducing effect of a hydrocarbon, in a gaseous or gasified condition, the said hydrocarbon containing not more than fifteen per cent. of nitrogen, the said hydrocarbon being highly heated previous to entrance in the reducing-chamber, substantially
20 as and for the purposes set forth.

9. An improved process for reducing zinc
25 oxidic ores, which consists in subjecting the material to the reducing effect of a hydrocarbon in a gaseous or gasified condition, the said hydrocarbon containing not more than fifteen per cent. of nitrogen, the said hydrocarbon being highly heated previous to entrance in the reducing-chamber, and in cooling
30 the resulting zinc-vapors in an atmosphere of such hydrocarbon, substantially as and for the purposes set forth.

10. An improved process for making spelter, which consists in subjecting zinc-containing
35 materials to the reducing effect of a mixture of gaseous or gasified hydrocarbons and water-gas heated previously to entrance in the

reducing-chamber, substantially as and for the purposes set forth.

11. An improved process for making spelter from zinc oxidic ores or zincic material,
40 which consists in reducing such material within a chamber solely by the action of heated gaseous or gasified hydrocarbons introduced within the chamber in a heated state, and in
45 cooling the resulting zinc-vapors in an atmosphere of such gas, substantially as and for the purposes set forth.

12. An improved process for making spelter from zinc oxidic ores, which consists in
50 subjecting the material to the reducing effect of gaseous or gasified hydrocarbons heated previously to entrance in the reducing-chamber, and in cooling the resulting zinc-vapors in an atmosphere of such gas, or carbon mon-
55 oxid formed by its destruction, substantially as and for the purposes set forth.

13. An improved process for making spelter from zinc oxidic ores or zincic material,
60 which consists in reducing such material within a chamber solely by the action of heated gaseous or gasified hydrocarbons injected within the chamber in a heated state, and in cooling the resulting zinc-vapors in an atmosphere of such gas, or carbon monoxid formed
65 by its destruction, substantially as and for the purposes set forth.

This specification signed and witnessed this
7th day of January, 1903.

OSKAR NAGEL.

Witnesses:

FRANK L. DYER,
JNO. ROBT. TAYLOR.