

UNITED STATES PATENT OFFICE

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METHOD FOR THE PRODUCTION OF NICKEL CARBONYL

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This invention relates to methods for the production of nickel carbonyl by passing carbon monoxide or gases containing carbon monoxide over metallic nickel. The invention is particularly applicable to the Mond process for the extraction of nickel from ores, mattes, residues or the like, in which process mattes or compounds containing nickel are reduced to yield metallic nickel which is treated with carbon monoxide, the reduction usually taking place at about 330° C. This process is carried on to a very large extent at the present time. The invention is, however, applicable generally to processes in which nickel carbonyl is formed from nickel by treatment with carbon monoxide and is either used as such or decomposed to yield nickel.

The primary object of the present invention is to increase the rate of formation of nickel carbonyl and thus to render the whole process more economical. A further object of the invention is to employ for this purpose simple and easily available materials. Other objects and advantages of the invention will hereinafter appear.

The invention is based upon the discovery that the rate of formation of nickel carbonyl is increased by the presence in the reaction chamber of a compound containing sulphur, selenium or tellurium in active form. This expression "active form" as used in this specification is intended to include compounds of sulphur, selenium and tellurium such for example as nickel sulphide, nickel selenide or nickel telluride which may be formed or introduced as hereinafter described, but does not include any sulphide originally present in the ore or in the matte after melting and allowed to remain as such up to the stage of formation of the carbonyl, since it is found that such sulphides do not exert the favourable promoting action of the invention. Again certain sulphur compounds such as lead sulphide mentioned below neither contain sulphur in active form nor react to produce under the conditions of reduction of reaction compounds containing sulphur in active form and their use is not, therefore, within the present invention.

Further it is found that if the sulphur-containing compounds, either before or after conversion to the form in which they are present in the reaction chamber, are subjected to such temperatures that sintering of the matte would normally take place, i. e. temperatures which may be of the order of 500° C. and upwards, the sulphur is not in active form in the reaction chamber and the beneficial action of the invention is not produced. Finally, of course, in the introduction or formation of the active sulphur, the introduction or formation of any body or element such as oxygen which would have a deleterious effect upon the formation of nickel carbonyl must be avoided. Thus for example a substance such as mercaptan which tends to deposit carbon on the nickel and thus to cover it so that it cannot react efficiently with carbon monoxide cannot be used, although mercaptan actually produces a compound containing sulphur in active form. It is, however, within the invention to use such a substance provided that steps are taken, as by adding simultaneously another substance capable of reacting with or fixing the deleterious body or element, to prevent that body or element being introduced into or formed in the reaction chamber so as to exert its deleterious effects.

It is not certain to what the promoting action of the invention is to be attributed, but it has been found in practice that when the process is carried on so that the sulphur, selenium or tellurium introduced into the reaction chamber is at least in part in the form of nickel sulphide, nickel selenide or nickel telluride, satisfactory results are obtained.

It is preferred to employ sulphur rather than selenium or tellurium and for the sake of convenience the process will be more fully described with reference to sulphur compounds and to the Mond process. It will be understood that in general where compounds of selenium or tellurium analogous to the sulphur compounds mentioned exist and act similarly in reactions other than those with which this invention is concerned, they may be employed in place of the sulphur compounds.

The presence of the active sulphur in the reaction chamber may be brought about by adding to the matte or reduced metal a sulphur-containing compound in solid form, or in the form of a liquid, solution, wet mixture or suspension; or by introducing small quantities of a sulphur-containing gas or vapour into the reaction chamber or by bringing the gas or vapour into contact with the matte at a previous stage of the process; or by allowing to remain or only partially removing sulphates or other sulphur-containing compounds formed in the matte prior to the reduction thereof but not originally present in the ore or matte.

As mentioned above it is found particularly advantageous in practice if compounds are added which are capable of producing nickel sulphide. Thus a substance such as nickel sulphate may be added to the matte prior to or during reduction. Again a sulphide, which may advantageously be nickel sulphide itself, may be added.

When the added compound is in the form of a liquid suspension or solution, preferably it is thoroughly incorporated with the material and the whole is then dried and ground before being passed to the reduction chamber.

Another method of carrying out the invention consists in moistening the matte with dilute sulphuric acid, so that sulphates are formed.

When sulphates are produced in the matte by calcination, or otherwise as by the addition of sulphuric acid after calcination, the normal process of removing them by washing may be stopped short or entirely omitted so that some or all are left and are reduced to sulphides in the reduction chamber. In the case of mattes which are not treated with sulphuric acid after calcination, steps are preferably taken in such a case to distribute the sulphates throughout the matte, since in the main they form on the surface of the matte. This distribution may be effected, for example, by wetting the calcined matte so as to carry inwards sulphates formed on the surface and then drying the matte. In practice, however, careful regulation of the calcination and washing operations are necessary to produce the desired amount of sulphates in this way.

When carrying on the novel process by the introduction of solid sulphides it is found that not every metallic sulphide has a beneficial effect upon the reaction. For example, although with a matte containing less than two per cent of copper, the sulphides of nickel, sodium, cobalt, iron, zinc, cadmium, mercury, calcium, copper (cupric), antimony, manganese, barium and arsenic all have a favourable effect, lead sulphide and cuprous sulphide added in similar quantities do not serve to produce compounds having sulphur in active form and thus produce

little, if any, beneficial effect. These two sulphides do not liberate or form under the conditions of operation any substance such as hydrogen sulphide or sulphur dioxide which could react with the reduced nickel to form a promoting body or could themselves act as promoting agents. All the beneficial sulphides mentioned above and phosphorus pentasulphide and selenium and tellurium sulphides which give good results should be added before or during the reduction process, except that nickel sulphide and mercury sulphide may be added to the actual reaction chamber. Even so, however, the effect produced with nickel and mercury sulphides is better if they are added before or during the reduction.

It has been found that the beneficial effect of the present invention is generally adversely affected by the presence of certain metals other than nickel in the matte, varying with nature and amount of such metals.

Thus, with a matte containing as much copper as fourteen per cent, only the sulphides of nickel, zinc and arsenic produce any substantial beneficial effect when added to the reduction chamber. On the other hand when sulphates are added to the reduction chamber, the percentage of copper in the matte has less influence upon the action, and with a matte containing fourteen per cent of copper, sulphates of nickel, zinc, aluminium, cadmium, mercury, copper and chromium, and also ferric sulphate, all produce a beneficial effect. The alkali and alkaline earth sulphates do not decompose in the reduction chamber to produce compounds containing sulphur in active form, but if the alkali sulphates are added in the form of alums before or during the reduction of the matte, the yield of nickel carbonyl is increased. In general a matte high in copper requires more sulphur than one low in copper.

When carrying on the process with the use of gases or vapours the gas or vapour may be passed over the reduced matte either before the latter is treated with carbon monoxide or at the same time as the carbon monoxide.

Hydrogen sulphide is most advantageously employed and it is found that the most beneficial results are obtained at temperatures below 150° C., the promoting action resulting from the introduction of hydrogen sulphide being considerably reduced at higher temperatures.

Sulphur dioxide may also advantageously be employed and may be added during or after reduction of the matte. It is found that improved results are obtained with sulphur dioxide if higher temperatures, of the order of 330° C., are employed. Some improvement is effected if sulphur dioxide is mixed with the carbon monoxide passing to the reaction chamber, but the yield of nickel car-

bonyl is not so good in this case as in the case of passing sulphur dioxide through the reduction chamber. Improved results are obtained if the matte is subjected to slight further reduction after treatment with sulphur dioxide, since by this means any nickel oxide formed is reduced.

Other gases or vapours which may be employed are carbon oxysulphide (COS), carbon disulphide (CS_2), or thiophene ($\text{C}_4\text{H}_4\text{S}$), all of which act in a similar manner to and may be employed similarly to hydrogen sulphide. Sulphur vapour also produces a distinct improvement in the rate of extraction of nickel when introduced either during or after reduction or into the actual reaction chamber, but the results obtained with this vapour are not as good as those obtained with hydrogen sulphide. Again such sulphur-containing compounds as sulphur chloride, allylisothiocyanate, benzene sulphonic acid, benzene sulphonic chloride and thioacetic acid may be employed and may be introduced into the reduction or reaction chamber in vapour form.

Gases may also be generated by the addition, in solid form, of thio-sulphates, thionates and so forth which give off sulphur-containing gases during the reduction process.

In the Mond process for extracting nickel it is known that the presence of certain other metals, in particular cobalt, has a detrimental effect on the nickel extraction. It is found that by the novel process, in particular when hydrogen sulphide is added, this detrimental effect is very considerably counteracted. Furthermore, the ill effects arising when the matte is reduced at too high a temperature are to some extent rectified by treatment with hydrogen sulphide.

It is preferred to carry on the novel process in such a way that the total amount of active sulphur present in the reaction chamber lies between 0.2 and 5% of the weight of the material introduced into the reduction chamber when solids or liquids are employed and between 0.05 and 5% when gases or vapours are employed, although owing to the presence in the matte of inactive sulphur in the form, for example, of sulphides which were originally present as such in the ore or in the matte after melting, the total sulphur content in the matte entering the reaction chamber may be greater. The figures given above are applicable in general to sulphates and sulphides, but when such substances as sodium sulphide or cobalt sulphide are added, a detrimental effect may be produced by the sodium or cobalt and consequently only small quantities should be used.

A few examples of the beneficial effect produced by the invention may be mentioned to illustrate the method of carrying out the invention. The addition of 1% of sulphur

in the form of nickel sulphate to a calcined matte containing 76.27% of nickel and cobalt, 1.85% of copper and 0.21% of sulphur increased the amount of nickel extracted in ten hours from 53.4% to 94.4%. In another case a calcined matte containing 61.8% of nickel and cobalt and 14.96% of copper was reduced with and without the addition of 5% of its weight of nickel sulphate crystals in solution. The addition of the nickel sulphate increased the amount of nickel extracted in five hours from 57.2% to 74.4%. In another case 100 kilogrammes of a calcined matte containing 74.1% nickel, 2.6% copper and 0.28% sulphur present as sulphates were thoroughly wetted with 14 litres of a solution of copper and nickel sulphates containing 97 grammes of copper and 83 grammes of nickel per litre. The resulting uniform mixture was thoroughly dried, the dry mass containing 1.5% sulphur in the form of sulphates. This was reduced and the rate of extraction of nickel from the matte was found to have been increased by 33% by the addition of the sulphate solution.

Again with sulphur-containing gases, in one case treatment with hydrogen sulphide gas at 50°C . of a calcined and reduced matte containing 73.34% of nickel and 1.12% of cobalt without any copper or sulphates increased the amount of nickel extracted in five hours from 16.8% to 86.4%. In another case treatment with carbon oxysulphide immediately before volatilization increased the percentage of nickel extracted from a matte in five hours from 55.3% to 86.8%. Again, by passing sulphur dioxide over a matte reduced at 330°C ., after the subsequent reduction, the yield of nickel carbonyl in five hours was increased from 31.1% to 59.9%.

As mentioned previously the compounds of selenium and tellurium analogous to those of sulphur described above may be employed, although in general selenium does not give such good results as sulphur and tellurium is not as good as selenium. In fact many tellurium compounds such as the tellurates are not truly analogous and do not produce active tellurium because they do not yield or serve to form tellurium oxide or hydrogen telluride, where the corresponding sulphur compounds yield or form sulphur dioxide or hydrogen sulphide. Further in cases where opposing effects are present, such for example as is the case with mattes high in copper, the beneficial effect produced by tellurium is so small as to be negligible. It is found, however, that hydrogen selenide gives results as good as hydrogen sulphide. Of course the methods of using selenium and tellurium compounds are not in every case the same as with the analogous sulphur compounds. For example since selenium dioxide is a solid whereas sulphur dioxide is a

gas, a different method of application is necessary.

Of course, in every case in order to extract nickel in the form of carbonyl in the most efficient manner, the actual nickel carbonyl formation must be carried on in the absence of air. Finally, although normally the process is carried on at atmospheric pressure, in some cases higher pressures or higher temperatures or both may be employed.

I claim:—

1. In a process for the extraction of nickel from ores, mattes, residues or the like which includes the formation of nickel carbonyl from reduced nickel and carbon monoxide in a reaction chamber, the method of increasing the rate of formation of nickel carbonyl which comprises carrying out the reaction in the reaction chamber in the absence of oxygen and in the presence of a compound containing a member of the sulphur group in active form.

2. In a process of forming nickel carbonyl from nickel and carbon monoxide, the method of increasing the rate of formation of nickel carbonyl which comprises carrying out the reaction in the absence of oxygen and in the presence of a compound containing a member of the sulphur group in active form.

3. In a process of extracting nickel from ores or mattes which includes the formation in a reaction chamber in the absence of oxygen of nickel carbonyl from nickel reduced at relatively low temperatures, the method of increasing the rate of formation of nickel carbonyl which comprises carrying out the reaction in the reaction chamber in the absence of oxygen and in the presence of a compound containing a member of the sulphur group in active form.

4. In a process for the extraction of nickel from ores, mattes, residues or the like which includes the formation of nickel carbonyl from reduced nickel and carbon monoxide in a reaction chamber, the method of increasing the rate of formation of nickel carbonyl which comprises introducing into the reaction chamber a solid compound containing a member of the sulphur group, the compound being in such form that a compound containing the member of the sulphur group in active form is present during the reaction, and carrying out the reaction in the absence of oxygen and in the presence of said last mentioned compound.

5. In a process for the extraction of nickel from ores, mattes, residues or the like which includes the formation of nickel carbonyl from reduced nickel and carbon monoxide in a reaction chamber, the method of increasing the rate of formation of nickel carbonyl which comprises introducing into the reaction chamber nickel sulphide in such form that a compound containing sulphur in active form is present during the reaction, and

carrying out the reaction in the absence of oxygen and in the presence of said last mentioned compound.

6. In a process for the extraction of nickel from ores, mattes, residues or the like which includes the formation of nickel carbonyl from reduced nickel and carbon monoxide in a reaction chamber, the method of increasing the rate of formation of nickel carbonyl which comprises adding to the matte or reduced metal a compound containing a member of the sulphur group in such form that a compound containing a member of the sulphur group in active form is present during the reaction, and thereafter treating the mixture in the absence of oxygen with carbon monoxide.

7. In a process for the extraction of nickel from ores, mattes, residues or the like which includes the formation of nickel carbonyl from reduced nickel and carbon monoxide in a reaction chamber, the method of increasing the rate of formation of nickel carbonyl which comprises adding to the matte a compound in liquid form capable of yielding under the conditions of reduction and reaction a compound containing a member of the sulphur group in active form, reducing the nickel in the matte, and thereafter treating the mixture in the absence of oxygen with carbon monoxide.

8. In a process for the extraction of nickel from ores, mattes, residues or the like which includes the formation of nickel carbonyl from reduced nickel and carbon monoxide in a reaction chamber, the method of increasing the rate of formation of nickel carbonyl which comprises adding to the matte a compound in liquid form capable of yielding under the conditions of reduction and reaction of yielding a compound containing a member of the sulphur group in active form, drying the mixture, grinding it, reducing the nickel in the mixture, and treating it in the absence of oxygen with carbon monoxide.

9. In a process for the extraction of nickel from ores, mattes, residues or the like which includes the formation of nickel carbonyl from reduced nickel and carbon monoxide in a reaction chamber, the method of increasing the rate of formation of nickel carbonyl which comprises reducing a mixture of the matte and nickel sulphate, and thereafter treating the reduced mixture in the absence of oxygen with carbon monoxide.

10. In a process for the extraction of nickel from ores, mattes, residues or the like which includes the formation of nickel carbonyl from reduced nickel and carbon monoxide in a reaction chamber, the method of increasing the rate of formation of nickel carbonyl which comprises reducing a mixture of the matte and a sulphide in such form that a compound containing sulphur in active form is present during the reaction in the

reaction chamber, and thereafter treating the reduced mixture in the absence of oxygen with carbon monoxide.

11. In a process for the extraction of nickel from ores, mattes, residues or the like which includes the formation of nickel carbonyl from reduced nickel and carbon monoxide in a reaction chamber, the method of increasing the rate of formation of nickel carbonyl which comprises reducing a mixture of the matte and a metallic sulphide in such form that a compound containing sulphur in active form is present during the reaction in the reaction chamber, and thereafter treating the reduced mixture in the absence of oxygen with carbon monoxide.

12. In a process for the extraction of nickel from ores, mattes, residues or the like which includes the formation of nickel carbonyl from reduced nickel and carbon monoxide in a reaction chamber, the method of increasing the rate of formation of nickel carbonyl which comprises reducing a mixture of the matte and nickel sulphide, the nickel sulphide being in such form that a compound containing sulphur in active form is present during the reaction in the reaction chamber, and thereafter treating the reduced mixture in the absence of oxygen with carbon monoxide.

13. In a process for the extraction of nickel from ores, mattes, residues or the like which includes the formation of nickel carbonyl from reduced nickel and carbon monoxide in a reaction chamber, the method of increasing the rate of formation of nickel carbonyl which comprises carrying out the reaction in the reaction chamber in the absence of oxygen and in the presence of a compound containing sulphur in active form, the amount of active sulphur being .2-5% by weight of the unreduced nickel-bearing material.

14. In a process for the extraction of nickel from ores, mattes, residues or the like which includes the formation of nickel carbonyl from reduced nickel and carbon monoxide in a reaction chamber, the method of increasing the rate of formation of nickel carbonyl which comprises carrying out the reaction in the reaction chamber in the absence of oxygen and in the presence of a gas containing a member of the sulphur group in active form.

15. In a process for the extraction of nickel from ores, mattes, residues or the like which includes the formation of nickel carbonyl from reduced nickel and carbon monoxide in a reaction chamber, the method of increasing the rate of formation of nickel carbonyl which comprises carrying out the reaction in the reaction chamber in the absence of oxygen and in the presence of a gas containing sulphur in active form.

16. In a process for the extraction of nickel from ores, mattes, residues or the like which

includes the formation of nickel carbonyl from reduced nickel and carbon monoxide in a reaction chamber, the method of increasing the rate of formation of nickel carbonyl which comprises carrying out the reaction in the reaction chamber in the absence of oxygen and in the presence of hydrogen sulphide.

17. In a process for the extraction of nickel from ores, mattes, residues or the like which includes the formation of nickel carbonyl from reduced nickel and carbon monoxide in a reaction chamber, the method of increasing the rate of formation of nickel carbonyl which comprises carrying out the reaction in the reaction chamber at a temperature below 150° C. in the presence of hydrogen sulphide and in the absence of oxygen.

18. In a process for the extraction of nickel from ores, mattes, residues or the like which includes the formation of nickel carbonyl from reduced nickel and carbon monoxide in a reaction chamber, the method of increasing the rate of formation of nickel carbonyl which comprises carrying out the reaction in the reaction chamber in the absence of oxygen and in the presence of a gas capable of producing a compound containing sulphur in active form, the amount of sulphur-containing gas being such that the quantity of active sulphur present in the reaction chamber is .05-5% by weight of the unreduced nickel-bearing material.

19. In a process for the extraction of nickel from ores, mattes, residues or the like which includes the formation of nickel carbonyl from reduced nickel and carbon monoxide in a reaction chamber, the method of increasing the rate of formation of nickel carbonyl which comprises carrying out the reaction in the reaction chamber in the absence of oxygen and in the presence of a gaseous compound containing hydrogen and a member of the sulphur group.

20. In the process of forming nickel carbonyl from nickel containing matte by treating the matte with carbon monoxide, the method of increasing the rate of formation of nickel carbonyl which comprises calcining the matte, adding nickel sulphate in solution, drying the mixture, reducing the mixture to convert nickel sulphate into nickel sulphide, and treating the reduced mixture in the absence of oxygen with carbon monoxide.

21. In the process of forming nickel carbonyl from mattes containing nickel and copper by treating the matte with carbon monoxide, the method of increasing the rate of formation of nickel carbonyl which comprises calcining the matte, adding a solution of nickel sulphate and copper sulphate, drying the mixture, reducing the mixture to form a mixture containing nickel sulphide and reduced nickel, and treating the reduced

mixture in the absence of oxygen with carbon monoxide.

22. In a process for the extraction of nickel from ores, mattes, residues or the like which includes the formation of nickel carbonyl from reduced nickel and carbon monoxide in a reaction chamber, the method of increasing the rate of formation of nickel carbonyl which comprises carrying out the reaction in the reaction chamber in the absence of oxygen and in the presence of sulphur dioxide.

23. In a process for the extraction of nickel from ores, mattes, residues or the like which includes the formation of nickel carbonyl from reduced nickel and carbon monoxide in a reaction chamber, the method of increasing the rate of formation of nickel carbonyl which comprises adding sulphur dioxide to the reduction chamber, passing the reduced mixture to the reaction chamber, and there carrying out the reaction in the absence of oxygen.

24. In a process for the extraction of nickel from ores, mattes, residues or the like which includes the formation of nickel carbonyl from reduced nickel and carbon monoxide in a reaction chamber, the method of increasing the rate of formation of nickel carbonyl which comprises carrying out the reaction in the reaction chamber in the absence of oxygen and in the presence of nickel sulphide as a catalyst.

25. In a process for the extraction of nickel from ores, mattes, residues or the like containing less than 2% of copper, which includes the formation of nickel carbonyl from reduced nickel and carbon monoxide in a reaction chamber, the method of increasing the rate of formation of nickel carbonyl which comprises carrying out the reaction in the reaction chamber in the absence of oxygen and in the presence of a sulphide of an element of the group consisting of nickel, sodium, cobalt, iron, zinc, cadmium, mercury, calcium, cupric copper, antimony, manganese, barium, arsenic, phosphorus, selenium, and tellurium.

26. In a process for the extraction of nickel from ores, mattes, residues or the like which includes the formation of nickel carbonyl from reduced nickel and carbon monoxide in a reaction chamber, the method of increasing the rate of formation of nickel carbonyl which comprises carrying out the reaction in the reaction chamber in the absence of oxygen and in the presence of a sulphide of a metal of the group consisting of nickel, zinc and arsenic.

27. In a process for the extraction of nickel from ores, mattes, residues or the like which includes the formation of nickel carbonyl from reduced nickel and carbon monoxide in a reaction chamber, the method of increasing the rate of formation of nickel carbonyl

which comprises carrying out the reaction in the reaction chamber in the presence of a gas of the group consisting of hydrogen sulphide, sulphur dioxide, carbon oxysulphide, carbon disulphide, thiophene, sulphur vapor, sulphur chloride, allylthiocyanate, benzene sulphonic acid, benzene sulphonic chloride and thioacetic acid.

In witness whereof I hereunto subscribe my name this 4th day of December, A. D. 1930.

CHRISTOPHER MAURICE WALTER GRIEB.

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