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SEPARATION OF METALS

Carl Müller, Mannheim, Leo Schlecht, Ludwigshafen-on-the-Rhine, and Emil Keunecke, Oppau, Germany, assignors to I. G. Farbenindustrie Aktiengesellschaft, Frankfort-on-the-Main, Germany

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The present invention relates to the separation of metals and more particularly to the separation in a substantially pure state of iron, nickel, cobalt, molybdenum, tungsten, or other base metals capable of forming carbonyls, from mixtures, such as ores, intermediate products and the like containing several of these elements in a free or combined state.

Numerous metallurgical processes are known for effecting such separation of metals, but all of them are attended with the disadvantage that they are very troublesome, usually requiring a very great number of different operations, and often do not give satisfactory results.

Now, the process according to the present invention makes use of a reaction which has not hitherto been thought of when aiming at a separation of metals of the kind hereinbefore defined. Use is made according to the present invention of the capacity of the aforesaid metals of reacting with carbon monoxide or gases containing carbon monoxide with the formation of metal carbonyls.

It has been known prior to the present invention that the aforesaid metals are capable of forming metal carbonyls. However, difficulties have often been experienced in carrying through this reaction, due on the one hand to the fact that some metallic materials of the aforesaid kind react very difficultly with carbon monoxide, and on the other hand due to the fact that some of the metal carbonyls are very liable to suffer decomposition. In view of this, it has been customary to select rather specific conditions for the production of metal carbonyls, which conditions vary substantially, more particularly as to temperature and pressure, for each of the various metal carbonyls to be produced. It would therefore seem impossible to find out conditions under which a plurality of metals, each of which is capable of forming a metal carbonyl, can be converted simultaneously into the corresponding metal carbonyls with a satisfactory yield and at a speed of reaction which allows of work on an industrial scale.

Contrary to expectation, we have found that the formation of metal carbonyls can be carried through successfully within a very broad range of temperatures and pressures. It is this discovery that the process according to the present invention is based upon.

As has been set forth in our application for Patent, Ser. No. 255,182, filed February 17th, 1928, of which this application is a continuation in part, we have found that the said metals which form carbonyls can be recovered separately, in a very simple manner, and practically completely, from mixtures containing several of them, even, for example, from very low-grade ores, by treating the mixtures, after, if necessary, a suitable preparatory treatment, with carbon monoxide, and separating the metals by way of the resulting carbonyls. The method of working according to the present invention consists in allowing the carbonyl compounds to be formed simultaneously, if desired after a suitable preliminary treatment of the initial material, preferably under elevated pressure, at an elevated temperature, which generally ranges between about 50° and about 400° C., but which may also be outside this range, since it depends on the pressure of the carbon monoxide, and then separating them by fractional dephlegmation, fractional distillation or other suitable method, after which they are decomposed into pure metals and carbon monoxide. All of these methods of separation of the carbonyls are equivalents for the purpose of the present invention and are hereinafter referred to for the sake of brevity as "fractionating".

According to the present invention, all substances which contain several metals capable of forming carbonyls as for example oxidic, sulphidic, and arseniferous ores, metallurgical intermediate or waste products, scrapings, sweepings, and speiss, can be treated. All that is necessary is to ensure, by suitable preliminary treatment, such as roasting and reduction, that the metals are present in the material to be treated with carbon monoxide in a reactive form.

We shall now proceed to explain more in detail the conditions under which we carry through the formation of the metal carbonyls.

This reaction may be carried through even at atmospheric pressures, though as a rule the use of higher pressures is advantageous, because then the speed of reaction is greater and there is less risk of a decomposition of the metal carbonyls taking place. The upper pressure limit is given only by the resistance of the apparatus used, and thus the process may be carried through at pressures as high as 50, 100, 200, 500 or even more atmospheres.

As has been pointed out above, the temperature usually ranges between about 50° and about 400° C. The lower temperatures within this range are used when treating materials which readily react with carbon monoxide, whereas higher temperatures within the order specified are employed for initial materials which react rather difficultly. In the case of difficultly re-

acting initial materials it is also advisable to use very high pressures.

We shall now explain more in detail by way of some specific examples, how the production of the metal carbonyls may be carried through in the process according to the present invention.

Example 1

a. A material containing the oxides of iron and nickel in addition to calcium sulphate is reduced by means of hydrogen at temperatures below 500° C., whereafter it contains 20 per cent, by weight, of iron and 20 per cent of nickel. This material is acted upon with a stream of carbon monoxide at 60° C. and atmospheric pressure. In the course of 3 days 80 per cent of the material is converted into the corresponding carbonyls.

b. The same reduced initial material is treated with a stream of carbon monoxide at 100° C. and under a pressure of 10 atmospheres. Within 10 hours 90 per cent of the material is converted into the corresponding carbonyls.

c. The same reduced initial material is acted upon with a stream of carbon monoxide at 200° C. and under a pressure of 200 atmospheres. Within an hour 98 per cent of the material is converted into the corresponding carbonyls.

Example 2

a. A material containing 12 per cent of iron, 6 per cent of nickel and 6 per cent of cobalt in a reactive form in addition to gangue is treated with a stream of carbon monoxide at 200° C. and under a pressure of 200 atmospheres. 90 per cent of the material is converted into the corresponding carbonyls in the course of 8 hours.

b. The same initial material is treated with a stream of carbon monoxide at 240° C. and under a pressure of 1000 atmospheres. In this case 90 per cent of the material is converted into the corresponding carbonyls in the course of 4 hours.

In these two experiments a mixture of metal carbonyls is first obtained which is comparatively rich in the carbonyls of iron and nickel, whereas later a carbonyl mixture comparatively rich in cobalt carbonyl is formed.

Example 3

a. An initial material which has been subjected to reduction and then contains 10 per cent of metallic iron, 22.5 per cent of metallic nickel and 40 per cent of metallic molybdenum is acted upon with a stream of carbon monoxide at 200° C. and under a pressure of 200 atmospheres. Thereby 85 per cent of the iron and nickel and 1 per cent of the molybdenum is converted into the corresponding carbonyls.

b. The same initial material is treated with a stream of carbon monoxide at 220° C. and under a pressure of 200 atmospheres. Thereby 85 per cent of the iron and nickel and 5 per cent of the molybdenum is converted into the corresponding carbonyls.

c. The same initial material is acted upon with a stream of carbon monoxide under a pressure of 200 atmospheres, while slowly increasing the temperature from 220° to 300° C., at the same rate as the formation of the carbonyls tends to decrease. At temperatures above 240° C. only small amounts of the carbonyls of iron and nickel are formed, but finally 13 per cent of the molybdenum is converted into carbonyl.

As will be seen from the foregoing examples the temperature and pressure should preferably be selected so that the material of lowest reactivity reacts with the carbon monoxide at a satisfactory speed. The same applies to the speed of the gas current and its percentage in carbon monoxide, in case a gas mixture containing carbon monoxide is used. Under such conditions also the more reactive metals are converted in a satisfactory manner. It is only when one component of the initial material is particularly reactive, whereas another component has a very low reactivity, that it is preferable to slowly increase the reaction temperature, whereby two fractions of metal carbonyls are obtained, of which the one is comparatively rich in the carbonyl of the highly reactive metal, the other being comparatively rich in the carbonyl of the other metal. Of course, care should be taken that practically no decomposition of the carbon monoxide takes place, and it is for this reason that the reaction temperature should preferably not exceed about 400° C.

In case the metals capable of forming metal carbonyls are present in the initial material in a form in which they do not react, or do not sufficiently rapidly react, with carbon monoxide, the initial material is first subjected to a suitable pretreatment in the manner which is well known in the art from the production of single metal carbonyls, and which therefore will not require detailed explanation. As examples of such preliminary treatments may be mentioned roasting followed, if necessary, by reduction in the case of, for example, natural sulphides such as nickel ores, or also oxidation and, if necessary, subsequent reduction.

We now come to the explanation of that step in our process which has been referred to above as "fractionating".

As has been set forth, this may be effected for example by fractional dephlegmation or fractional distillation. Regard must be had in this step to the properties of the several metal carbonyls, which are well known in the art, to avoid a decomposition of the metal carbonyls. Accordingly, the separation of the carbonyls by distillation is preferably effected in an atmosphere of stagnant or of flowing carbon monoxide which will prevent decomposition, and if desired under elevated pressure.

Another method of "fractionating" consists in effecting the separation of the metal carbonyls by freezing out, if desired in the presence of solvents, in which latter case the separation is effected by fractional crystallization. This method of "fractionating" is based upon the surprising discovery that the solubility of solid metal carbonyls in liquid metal carbonyls strongly decreases as the temperature is reduced, and that from the liquid mixtures pure metal carbonyls crystallize and not, as might be expected, mixed crystals of several metal carbonyls. The solid metal carbonyls which have separated out, can easily be separated from the liquid substances present, as for example by decantation, filtration or centrifuging, and may then be decomposed to the free metals either directly or preferably after any adhering liquid metal carbonyls have been removed by means of, preferably cooled, solvents. By the said method it is also possible to separate several solid metal carbonyls such as those of cobalt and molybdenum, either simultaneously or one after the other, from one or more liquid metal carbonyls, as for example mixtures of iron carbonyl and nickel carbonyl. Mixtures of solid metal carbonyls thus obtained may then be separated further for example by fractional distillation.

In some cases and especially when the mixture to be separated contains large amounts of metal carbonyls of higher melting point such as cobalt carbonyl and only small quantities of metal carbonyls of low melting point such as nickel carbonyl, it is advantageous to dissolve the mixture in solvents such as benzene, benzine, tetrahydronaphthalene or carbon tetrachloride, and then to crystallize the difficultly soluble carbonyl or carbonyls by cooling the solution.

"Fractionating" may also be effected in any other suitable manner, as for example by fractional decomposition, fractional absorption, fractional diffusion, fractional sublimation, or also by extraction.

The following examples will serve to further explain the "fractionating" step.

Example 4

A mixture of equal parts, by weight, of iron carbonyl and nickel carbonyl is heated at atmospheric pressure on a water bath kept at 80° C., while passing through a current of carbon monoxide. The vapors evolved are passed through a fractionating column. At 28° C. practically pure nickel carbonyl distils off, pure iron carbonyl being left in the distilling vessel.

Example 5

A mixture of 30 per cent, by weight, of cobalt carbonyl and 70 per cent, by weight, of nickel carbonyl is heated at atmospheric pressure on a water bath kept at 80° C., while passing through a current of carbon monoxide. The vapors evolved are passed through a fractionating column. At 30° C. practically pure nickel carbonyl distils off, pure cobalt carbonyl being left in the distilling vessel.

Example 6

A mixture of equal parts, by weight, of iron carbonyl and cobalt carbonyl is heated on a water bath in vacuo under a pressure of 25 millimeters mercury column, while passing through a current of carbon monoxide. The vapors evolved are passed through a fractionating column. At 30° C. practically pure iron carbonyl distils off, cobalt carbonyl with only about 0.2 per cent of iron carbonyl being left in the distilling vessel.

Example 7

A mixture of 65 parts, by weight, of iron carbonyl, 30 parts, by weight, of nickel carbonyl and 5 parts, by weight, of cobalt carbonyl is filtered and then distilled at atmospheric pressure. The vapors evolved are passed through a fractionating column. At a temperature, in the dephlegmator of the column, of 42° C. pure nickel carbonyl distils over. The second fraction which is obtained at 102° C. consists of pure iron carbonyl. The residue left in the distillation vessel consists of cobalt and the difficultly volatile cobalt tri-carbonyl and contains only small amounts of iron or iron compounds.

Example 8

A mixture of equal parts, by weight, of iron carbonyl and cobalt tetracarbonyl is heated to 120° C. under a pressure of 20 atmospheres in a distilling vessel provided with a fractionating column, while passing through a current of carbon monoxide. Pure iron carbonyl distils off, cobalt tetracarbonyl with only about 0.3 per cent of iron carbonyl being left in the distillation vessel.

Example 9

2 parts, by weight, of a mixture of 96 per cent, by weight, of cobalt carbonyl and 4 per cent, by weight, of nickel carbonyl are cooled to 12° below zero C. and are shaken twice each with 1 part of benzine likewise cooled to 12° below zero C. The benzine is poured off and the solid cobalt carbonyl obtained is freed from benzine by suction while excluding air. 77 per cent of the cobalt carbonyl originally present are thus obtained in a crystallized form practically free from nickel. The remainder of the cobalt carbonyl can be recovered from the benzine solution by distilling off the benzine and the nickel carbonyl in a current of carbon monoxide.

Example 10

A slow current of carbon monoxide is passed at 115° C. and under a pressure of 10 atmospheres through a mixture of 40 parts, by weight, of cobalt carbonyl and 60 parts, by weight, of iron carbonyl. A suspension of cobalt and cobalt tricarbonyl in iron carbonyl is formed, which is then allowed to cool. The solid constituents of the suspension are filtered off and washed with a little tetrahydronaphthalene. Iron carbonyl containing only small amounts of cobalt carbonyl is obtained. The mixture of cobalt and cobalt tricarbonyl is subjected to thermal decomposition, whereby metallic cobalt containing only traces of iron is obtained.

It will be seen from the foregoing that it is possible according to the present invention to produce pure or practically pure metal carbonyls. In case the free metals are to be produced, the metal carbonyls are then subjected to thermal decomposition in any known or suitable manner, as for example according to the U. S. Patents Nos. 1,757,659 and 1,759,661.

While it will be clear from the foregoing, how the several steps of our process are carried out in practice, the whole series of steps will become still clearer by the following examples.

Example 11

White nickel ore (chloanthite) is heated to 550° C. in a current of air and steam, to drive off sulphur and arsenic, and is then reduced in a current of hydrogen at 450° C. The reduced ore is next treated with a current of carbon monoxide at 140° C. and under a pressure of 180 atmospheres. The resulting reaction gas is passed through a receiver cooled to −20° C. in which a mixture of the carbonyls of nickel, iron and cobalt condenses. During the distillation of this mixture in a current of carbon monoxide at ordinary pressure, nickel carbonyl, containing 2.5 per cent of iron carbonyl, passes over first, at from 20° to 45° C., followed at from 45° to 60° C., by a mixture of 66.8 per cent of nickel carbonyl and 33 per cent of iron carbonyl. The pure compounds are obtained by subjecting these liquid carbonyl mixtures to a second fractional distillation at atmospheric pressure.

The residue from the first distillation consists of a mixture of cobalt tricarbonyl and cobalt tetracarbonyl, which is free from nickel and iron carbonyl, but contains small quantities of solid impurities carried over from the reaction furnace. It is converted into pure tetracarbonyl in a current of carbon monoxide at 150° C. and under a pressure of 200 atmospheres and this product is

then volatilized, thereby separating it from the other impurities. Condensation is effected under the same elevated pressure of carbon monoxide in a receiver cooled to 0° C. On decomposing the recovered pure carbonyls of nickel, cobalt and iron by heat, the metals are obtained in a high state of purity.

Example 12

A metallurgical waste sludge containing cobalt, iron, and zinc is reduced with coal and then acted upon with carbon monoxide at 150° C. and under a pressure of 200 atmospheres. The resulting mixture of the carbonyls of iron and cobalt is withdrawn from the high pressure apparatus in the liquid state at 55° C. and collected in a receiver cooled by means of a mixture of ice and common salt. 75 per cent of the cobalt carbonyl crystallize from the liquid mixture and are separated therefrom by decantation and filtration by suction. The cobalt carbonyl thus obtained is practically pure. The liquid portion of the carbonyl mixture may serve for taking up further batches of the carbonyl mixture withdrawn from the high pressure apparatus.

Example 13

An initial material containing 13 per cent of iron and 20 per cent of nickel in a reactive form is acted upon with a stream of carbon monoxide at between 200° and 250° C. and under a pressure of 300 atmospheres. 90 per cent of the metals are converted into the carbonyls. The resulting carbonyl mixture is preheated to 60° C. and then injected into the middle part of a bell-tray column provided with a dephlegmator regulated to reflux twice the amount of the distillate leaving the column. In the upper part of the column a temperature of 42° C. is maintained, while the temperature in the lower part of the column is 102° C. Pure nickel carbonyl is withdrawn at the top, and pure iron carbonyl at the bottom of the column. Only small amounts of a non-volatile residue are left which contains mainly oil in addition to small quantities of metals and decomposition products of metal carbonyls; this residue may be worked up by combustion, reduction and conversion into metal carbonyls.

While we have explained the process according to the present invention by reference to specific examples, we wish it to be understood that our invention is not limited thereto, the scope of the invention being defined by the appended claims.

What we claim is:

1. The process for the separate recovery of base metals capable of forming metal carbonyls from a material containing at least two of such metals, which comprises acting on said material, while the same contains the said metals in a form capable of reacting with carbon monoxide, with carbon monoxide under conditions causing reaction of at least two of said metals, thereby forming the carbonyl compounds of said metals simultaneously, and "fractionating" the resulting carbonyl mixture.

2. The process for the separate recovery of base metals capable of forming metal carbonyls from a material containing at least two of such metals, which comprises acting on said material, while the same contains the said metals in a form capable of reacting with carbon monoxide, with carbon monoxide under conditions causing reaction of each of said metals, thereby forming the carbonyl compounds of said metals simultaneously, and "fractionating" the resulting carbonyl mixture.

3. The process for the separate recovery of base metals capable of forming metal carbonyls from a material containing at least two of such metals, which comprises acting on said material, while the same contains the said metals in a form capable of reacting with carbon monoxide, with carbon monoxide at a temperature between about 50° and about 400° C. under conditions causing reaction of at least two of said metals, thereby forming the carbonyl compounds of said metals simultaneously, and "fractionating" the resulting carbonyl mixture.

4. The process for the separate recovery of base metals capable of forming metal carbonyls from a material containing at least two of such metals, which comprises acting on said material, while the same contains the said metals in a form capable of reacting with carbon monoxide, with carbon monoxide at a temperature between about 50° and about 400° C. under conditions causing reaction of each of said metals, thereby forming the carbonyl compounds of said metals simultaneously, and "fractionating" the resulting carbonyl mixture.

5. The process for the separate recovery of base metals capable of forming metal carbonyls from a material containing at least two of such metals, which comprises acting on said material, while the same contains the said metals in a form capable of reacting with carbon monoxide, with carbon monoxide under conditions causing reaction of each of said metals, thereby forming the carbonyl compounds of said metals simultaneously, and fractionally distilling the resulting carbonyl mixture.

6. The process for the separate recovery of base metals capable of forming metal carbonyls from a material containing at least two of such metals, which comprises acting on said material, while the same contains the said metals in a form capable of reacting with carbon monoxide, with carbon monoxide at a temperature between about 50° and about 400° C. under conditions causing reaction of each of said metals, thereby forming the carbonyl compounds of said metals simultaneously, and fractionally distilling the resulting carbonyl mixture.

7. The process for the separate recovery of base metals capable of forming metal carbonyls from a material containing at least two of such metals, which comprises acting on said material, while the same contains the said metals in a form capable of reacting with carbon monoxide, with carbon monoxide under conditions causing reaction of each of said metals, thereby forming the carbonyl compounds of said metals simultaneously, and fractionally distilling the resulting carbonyl mixture in an atmosphere of carbon monoxide.

8. The process for the separate recovery of base metals capable of forming metal carbonyls from a material containing at least two of such metals, which comprises acting on said material, while the same contains the said metals in a form capable of reacting with carbon monoxide, with carbon monoxide at a temperature between about 50° and about 400° C. under conditions causing reaction of each of said metals, thereby forming the carbonyl compounds of said metals simultaneously, and fractionally distilling the resulting carbonyl mixture in an atmosphere of carbon monoxide.

9. The process of separating iron, nickel and

cobalt from materials containing the same, which comprises treating said materials to place the above metals in a condition in which they will react with carbon monoxide, passing carbon monoxide over the so treated materials at a temperature of about 140° C. and a pressure of about 180 atmospheres, cooling the resulting gas mixture to condense the carbonyls of said metals, and subjecting the condensate to a fractional distillation to separate the iron, nickel and cobalt carbonyls respectively.

10. The process as defined in claim 9 wherein the fractional distillation is effected by distilling off nickel carbonyl at a temperature of from 20° to 45° C. and then distilling off the remaining nickel carbonyl and the iron carbonyl at a temperature of from 45° to 60° C. in a stream of carbon monoxide.

11. The process for the separate recovery of base metals capable of forming metal carbonyls from a material containing at least two of such metals, which comprises acting on said material, while the same contains the said metals in a form capable of reacting with carbon monoxide, with carbon monoxide under conditions causing reaction of each of said metals, thereby forming the carbonyl compounds of said metals simultaneously, and fractionally crystallizing the resulting carbonyl mixture.

12. The process for the separate recovery of base metals capable of forming metal carbonyls from a material containing at least two of such metals, which comprises acting on said material, while the same contains the said metals in a form capable of reacting with carbon monoxide, with carbon monoxide at a temperature between about 50° and about 400° C. under conditions causing reaction of each of said metals, thereby forming the carbonyl compounds of said metals simultaneously, and fractionally crystallizing the resulting carbonyl mixture.

13. The process for the separate recovery of base metals capable of forming metal carbonyls from a material containing at least two of such metals, which comprises acting on said material while the same contains the said metals in a form capable of reacting with carbon monoxide, with carbon monoxide under conditions causing reaction of each of said metals, thereby forming the carbonyl compounds of said metals simultaneously, and fractionally decomposing the resulting carbonyl mixture.

14. The process for the separate recovery of base metals capable of forming metal carbonyls from a material containing at least two of such metals, which comprises acting on said material, while the same contains the said metals in a form capable of reacting with carbon monoxide, with carbon monoxide at a temperature between about 50° and about 400° C. under conditions causing reaction of each of said metals, thereby forming the carbonyl compounds of said metals simultaneously, and fractionally decomposing the resulting carbonyl mixture.

CARL MÜLLER.
LEO SCHLECHT.
EMIL KEUNECKE.