Patented Feb. 16, 1943 2,311,307

UNITED STATES PATENT OFFICE

2,311,307

PRODUCTION OF METAL CARBONYLS

Rudolf Staeger, Ludwigshafen-on-the-Rhine, Peter Assmann, Berlin, and Kurt Ehrmann, Mannheim, Germany, assignors, by mesne assignments, to General Aniline & Film Corporation, New York, N. Y., a corporation of Delaware

No Drawing. Application January 26, 1940, Serial No. 315,780. In Germany October 13, 1938

4 Claims. (Cl. 23—203)

The present invention relates to improvements in the production of metal carbonyls.

The reaction between carbonyl-forming metals and carbon monoxide used for the technical production of metal carbonyls proceeds the more rapidly the more finely divided the state of the metal exposed to the action of the carbon monoxide. In order to obtain suitable finely divided metals, various methods have been proposed and in part employed, as for example the reduction of metal oxides by gases, especially at low temperatures, if desired with an addition of substances which prevent sintering, or the decomposition of the corresponding amalgams at low temperatures. It is also known that the content of carbonyl-forming metals in sulphur-containing smelting products, so-called mattes, is very readily converted into carbonyl by a treatment with carbon monoxide, especially under pressure, even when the said mattes are not in a finely divided state. Since the reactivity of such smelting products approximately corresponds to that to finely divided metals, but their weight per unit of volume is higher, their use offers economic advantages. Disadvantages are the troublesome development of sulphur-containing gases in the preparation of the smelting products and the formation of carbon oxysulphide which occurs in the treatment with carbon monoxide of materials rich in sulphur under very high pressures.

We have now found that the said disadvantages may be obviated while retaining the said advantages of a great reactivity and favorable space filling by starting from substantially sulphur-free smelting products which during their preparation have been activated with sulphur-free substances which while cooling the melt, are deposited on the grain boundaries of the metal. A specially suitable activator for the carbonyl formation is oxygen which leads to the formation of oxides which are deposited on the grain boundaries of the metal during the solidification of the melts. Also arsenic and bismuth may be employed as activators. Whereas for instance nickel sheet loses only 7.2 per cent of its weight in the form of carbonyl when treating it for 6 hours with carbon monoxide at 220° C. under a pressure of 200 atmospheres, an addition of 10 per cent of bismuth to molten nickel increases the reactivity of the nickel to such a degree that 80.5 per cent of the bismuth-containing nickel are volatilized in the form of carbonyl under the same conditions. Ready-formed oxides may also be added to the melts. By an addition of a small percentage, e. g. 5 per cent, of nickel oxide to a nickel melt, the reactivity of the nickel is considerably increased. A mixture of iron oxide with an amount of carbon insufficient for a complete reduction of the said oxide may be fused together, in order to obtain a suitable initial material for the production of iron carbonyl.

Furthermore oxidic materials substantially free from carbonyl-forming metals, such as kieselguhr or the like, exert a favorable activating effect.

The deposition of the substances added or formed during the smelting on the grain boundaries can be asisted in many cases by a thermal treatment.

The following examples will further illustrate how the said invention may be carried out in practice but the invention is not restricted to these examples. The parts are by weight.

Example 1

Massive iron metal is treated for 60 hours at 200° C. with carbon monoxide under a pressure of 200 atmospheres. It is scarcely attacked.

If, however, iron powder is fused in the air and the resulting iron is subjected in the form of pieces to the treatment with carbon monoxide under the said conditions, 8 per cent of the iron volatilizes as carbonyl.

If 10 parts of iron oxide are added to 100 parts of molten iron, then by treatment of the solidified mass under the said conditions with carbon monoxide 76 per cent of the material volatilizes in the form of iron carbonyl, i. e. more than 90 per cent of the iron originally present as metal; the residue mainly consists of iron oxide.

Example 2

5 and 10 parts of kieselbuhr are added respectively to two melts each of 100 parts of iron and after cooling each of the masses is treated with carbon monoxide as described in Example 1. 25 and 35 per cent of the material respectively are converted into iron carbonyl.

Example 3

Massive nickel metal is treated at 160° C. with carbon monoxide under a pressure of 100 atmospheres for 3 hours; 2.1 per cent of the nickel volatilizes in the form of nickel carbonyl.

If on the other hand nickel powder is fused in the air, 26.8 per cent of the nickel are volatilized as carbonyl by treatment with carbon monoxide under the said conditions. If the for-

mation of oxide is effected by blowing air into the melt and the melt is slowly cooled, the material can be broken under tha hammer and shows a grey fracture. When treating this material in the form of pieces with carbon monoxide under the same conditions, 50 per cent of the nickel volatilizes as carbonyl.

What we claim is:

1. A proces of producing metal carbonyls which comprises reacting carbon monoxide upon a substantially sulfur-free product solidified from a melt which contains a carbonyl-forming metal that has been activated by the deposition of a subordinate amount of an oxide on the grain boundaries of said carbonyl-forming metal during the cooling of the melt.

2. A process of producing metal carbonyls by reacting a carbonyl-forming metal with carbon monoxide which comprises melting a carbonyl-forming metal substantially free from sulphur, acting with oxygen upon the melt to form subordinate amounts of the oxide of the said metal, cooling the melt and subjecting the solidified mass to the action of carbon monoxide to form the carbonyl.

3. A process of producing metal carbonyls by reacting a carbonyl-forming metal with carbon monoxide which comprises melting a carbonyl-forming metal substantially free from sulphur, acting with air upon the melt to form subordinate amounts of the oxide of the said metal, cooling the melt and subjecting the solidified mass to the action of carbon monoxide to form the carbonyl.

4. A process of producing metal carbonyls by reacting a carbonyl-forming metal with carbon monoxide which comprises melting a carbonyl-forming metal substantially free from sulphur, adding to the melt subordinate amounts of an oxide which are deposited on the grain boundaries of the solidified metal, cooling the melt and subjecting the solidified mass to the action of the carbon monoxide to form the carbonyl.

RUDOLF STAEGER.
PETER ASSMANN.
KURT EHRMANN.