

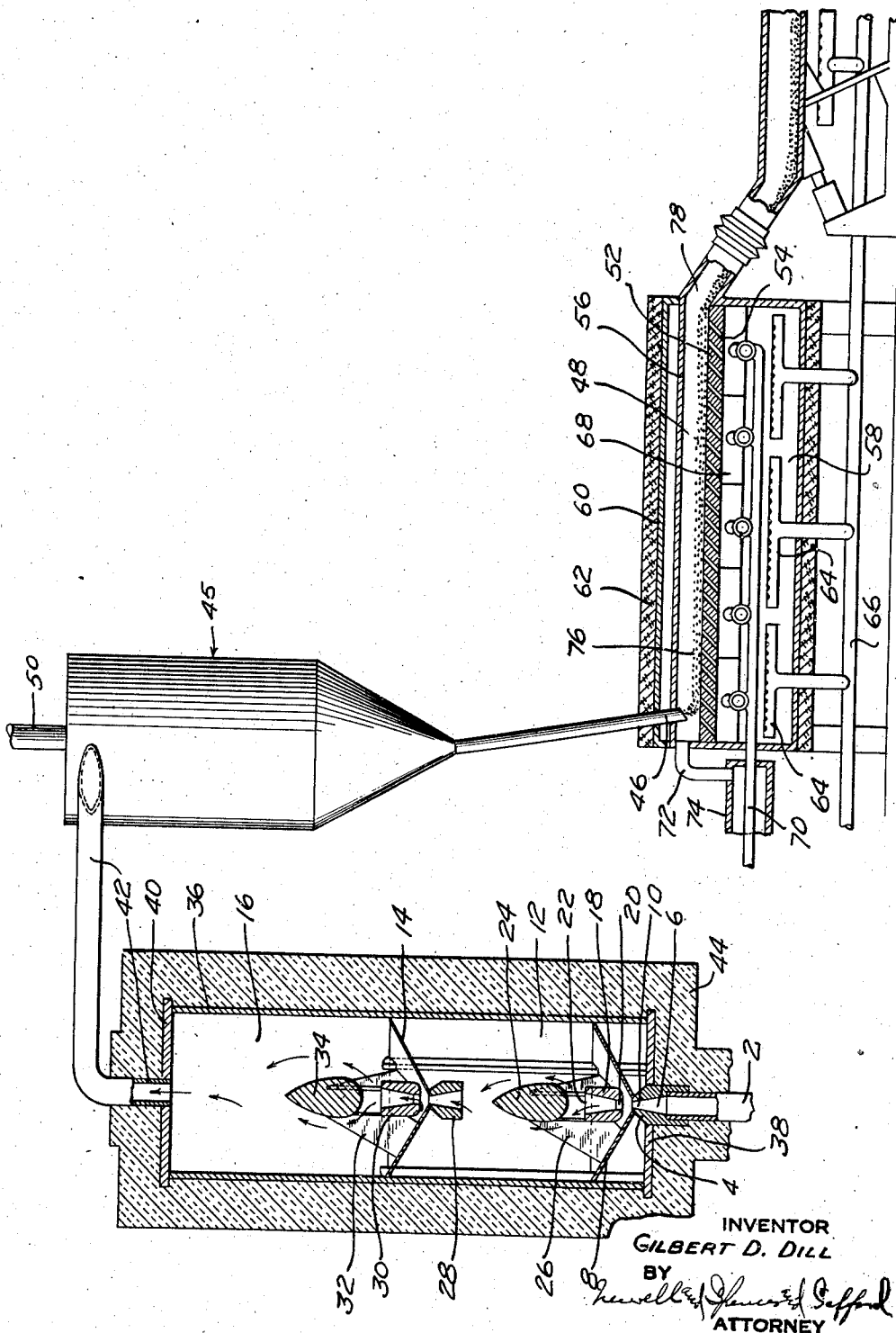
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PROCESS OF REDUCING METALLIC OXIDES

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## PROCESS OF REDUCING METALLIC OXIDES

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4 Claims. (Cl. 75-89)

This invention relates to the direct reduction of metals from their oxides or other compounds, and particularly to the preparation of metal oxides or other metal compounds for direct reduction.

In the direct reduction of metallic oxides at temperatures below the melting point of the metal, it is important, since the metal, after reduction, will usually maintain substantially the physical form or frame in which it exists in the oxide, that the reducing agent be brought into intimate association with the various parts of the oxide in order that it may perform its oxygen removing function throughout all parts of the metal skeleton. Many processes of effecting direct reduction of metals from their oxides, heretofore devised, have failed, when it has been attempted to practice them upon a commercial scale, because it has been impossible, in commercial scale operations, to secure the intimate association of the reducing agent with the various parts of the oxide requisite to complete reduction.

The present invention aims to take advantage of the catalytic characteristics of certain metallic compounds, either as they appear in nature or in forms to which they can readily be converted, to procure, by a preliminary treatment in which advantage is taken of the catalytic activity of the metallic compounds, such an intimate association of the reducing agent with the metallic compound that, when the compound is later subjected to reducing conditions, a quick, complete and clean reduction will take place.

It has been established that compounds of metals of the iron group, and particularly the oxides of iron, nickel, cobalt, and manganese, have the capacity, when brought into contact with hydrocarbon oils heated to temperatures in what is known as the catalytic cracking range of such hydrocarbon oils, which temperatures may range from 700° to 1000° F. for different oils, to effect a cracking of these oils with a considerable decomposition of the heavier constituents thereof and a resultant deposition of carbon, almost in molecular form. Such catalytic activity of metals of the iron group extends also to cracking and/or decomposition of some of the hydrocarbons present in natural gases. Moreover, it is not confined to compounds in which only one of the metals is present but is also exhibited by complex compounds including two or more of the metallic elements.

Because of the porous nature of the oxides of metals of the iron group as they appear in nature, and even in some of their artificial forms, and

also because of the presence of numerous cleavage planes, this catalytic cracking and decomposition will result in the carbon, which is released by the catalytic decomposition, being deposited not only upon but also within the oxides, substantially completely filling the pores and interstices thereof. If the oxides have been ground or otherwise brought into a fairly finely divided condition, not only will this catalytic reaction between the oxide and the heated hydrocarbon result in the particles of the oxide being given a protective coating of carbon to prevent sintering or sticking at the temperatures to which they are subjected in the ensuing reduction operation, but both the coating carbon and the carbon which has penetrated into the pores of or spaces within the oxide will be in such intimate association with the oxide that when the oxide is raised to the reducing temperature the carbon will immediately react with the oxygen of the oxide and effect a rapid and complete reduction thereof.

The invention aims not only to improve the treatment of metallic oxides preparatory to direct reduction, but also so to effect such treatment that the hydrocarbon employed to furnish the reducing reagent may itself be improved in composition by the catalytic treatment which has decomposed and/or cracked and/or to some extent reformed its higher boiling point constituents. Furthermore, the invention contemplates so carrying out the catalytic impregnation treatment as to provide or to assist in providing reducing gases for use in later stages of the process and also improved fuels for maintaining the required reaction temperatures.

Among the particular objects of the invention is to insure the bringing of the finely divided metallic oxide and the hydrocarbon into such intimate association with each other and under such conditions, particularly of temperature, that the desired decomposition and hydrocarbon reforming reaction will take place. A further object of the invention is to insure the maintenance of the intimate association until the desired impregnation of the oxide with the carbon resulting from the decomposition has taken place.

Other objects and important features of the invention will appear from the following description in which the manner of practicing the invention is particularly described in its application to the carbon impregnation and/or coating of oxides of iron. It will be understood, however, that the invention is not restricted to the preparation of iron ores or oxides for the final reducing step but that, with slight variations in the physical

conditions surrounding the reaction, the invention is equally applicable to the preparation of the ores or oxides of nickel, cobalt and manganese for the final reducing step and also to the preparation for reduction of any other metal oxides or mixtures of metal oxides which have the requisite capacity for catalytically decomposing hydrocarbons.

In preparing iron ore for treatment by the process of the present invention, the ore will be cleaned and crushed to that degree of fineness necessary for the removal of the gangue to the desired degree, which in most cases will be from 60 mesh up to 100 mesh or even finer, depending upon the character of the ore. From this crushed and now finely divided ore substantially all of the gangue or impurities will be removed by any of the known methods of concentration suitable to the particular type of ore, such as the magnetic separation employed with ores comprising principally the magnetic oxide  $Fe_3O_4$ . Other known methods may be employed in concentrating the ores comprising principally ferric oxide,  $Fe_2O_3$ .

The ore, having been concentrated until it consists mainly of  $Fe_2O_3$  or  $Fe_3O_4$  or of mixtures of these oxides, is then thoroughly heated and brought to the temperature most suitable for effecting the partial decomposition or cracking of the particular hydrocarbon to be used in effecting the carbon impregnation and/or coating of the ore. With an iron oxide as the catalytically active oxide to be treated and with a hydrocarbon oil having, among its constituents, high boiling point hydrocarbons, decomposition will begin in the neighborhood of 800° F. and the ore may, therefore, be heated to that temperature.

The selected hydrocarbon oil will also be heated to substantially the same temperature, that is 800° F., at which temperature it will be converted into a vapor, and the heated ore and the heated vapor will then be brought into such intimate association with each other that the catalytically induced reaction will take place and some at least of the constituents of the hydrocarbon will be decomposed, leaving free carbon within the pores, recesses and interstices or cleavage planes of the iron oxide. The decomposition will usually be accompanied by cracking of some of the hydrocarbons into lower boiling point hydrocarbons which can be separated in fractionating towers in the form of more marketable petroleum products, such as gasoline. The heavier portions which have not been decomposed or cracked in their first passage through the reaction zone may be recirculated.

In order to effect the desired intimate association and to maintain it for a sufficiently long time to secure the desired impregnation, the process is preferably practiced in apparatus in which the finely divided ore may be entrained in a stream of the hydrocarbon vapor, which is brought into a turbulent state, and in which the ore, by partaking of the turbulent movements of the hydrocarbon vapor, is caused to be thoroughly commingled therewith and thus brought into and maintained in reactive relation thereto.

A suitable apparatus for effecting the desired commingling and interaction of the finely divided ore and the hydrocarbon vapor is that described in my co-pending application Serial No. 244,612, filed December 8, 1938, and in my co-pending application Serial No. 341,478 filed June 20, 1940, which is a continuation in part of application Serial No. 244,612 in which provision is made for

bringing a fluid such as the hydrocarbon vapor here employed into a turbulent state by causing it to flow through successive zones of higher than average velocity and lower than average pressure and of lower than average velocity and higher than average pressure. The finely divided material, such as the oxide to be treated, may be entrained in the fluid to partake of the turbulent movements thereof. In this apparatus of my co-pending application, a thorough commingling of the hydrocarbon vapor and the finely divided oxide can be effected. A selective recycling is also provided for, thus insuring that every particle of the oxide, from the finest to the largest, will be sufficiently coated and/or impregnated with carbon to bring about the desired rapid and complete reduction when raised to the reducing temperature of metallic oxide upon which the process is being practiced.

In the accompanying drawing is illustrated apparatus for practicing the novel process of the present invention.

Referring to the drawing, the vaporized and preheated hydrocarbon, having the preheated finely divided ore entrained therein, is introduced into the intake pipe 2 of reaction apparatus such as disclosed in my co-pending application Serial No. 244,612. The intake pipe 2 has connected to its upper end one section 4 of a venturi, the section 4 having a comparatively steeply tapering interior passage 6 to produce the desired increase in velocity and reduction in pressure of the inflowing fluid. The upper end of the section 4 of the venturi passes through the bottom of an inverted frusto-conical partition or baffle 8 and, to permit making the opening in the baffle 8 not much larger than the outlet of the passage 6, the outer face of the section 4 may be tapered substantially to an edge where it meets the upper end of the substantially straight throat 10 in the upper part of the passage 6.

The inverted frusto-conical partition or baffle 8 forms the bottom of the lower reaction chamber 12 and a similar partition or baffle 14 forms the bottom of the upper reaction chamber 16. Each of these frusto-conical partitions or baffles 8 and 14 also serves as a hopper-like structure to direct the vaporized hydrocarbon and any entrained ore to be re-circulated to the low pressure part of the venturi, more fully to be described hereinafter.

Positioned above the upper end of the section 4 of the venturi is a section 18 in which is formed the expansion end of the venturi, the section 18 having at its lower end a bell-mouthed opening 20, this lower end of the section 18 being spaced from the upper end of the section 4 sufficiently to provide an annular passage into the passage through the venturi. The conical or bell-mouthed lower end 20 of the passage through the section 18 communicates at its upper end with the expansion passage 22 of the venturi which discharges into the reaction chamber 12. Located above the expansion passage 22 of the venturi and preferably in coaxial alignment therewith is a streamlined baffle 24 of substantially the ideal streamlining of a tear drop. This baffle 24 is supported by sheet metal supports 26 carried by the partition member 8 and spaced 120° apart. These supports 26 also carry the upper section 18 of the lower venturi.

Carried by the frusto-conical partition member 14 is the lower section 28 of a second venturi bearing the same relation to the partition 14 that

the section 4 bears to the partition 8. The upper member 30 of the upper venturi is of the same construction as the member 18 of the lower venturi and is supported in the same relation to the partition member 14 by supports 32 as is the member 18 in respect to the partition member 8 by its supports 26. The supports 32 for the Venturi member 30 also carry a streamlined baffle 34 of the same construction and arrangement with respect to its associated venturi as the baffle 24.

The side wall of the chambers 12 and 16 is formed by a cylindrical casing member 36 closed by end members 38 and 40, the end member 38 being provided with an opening in which the section 4 of the lower venturi is fitted and the end member 40 being provided with an opening in which the discharge pipe 42 is fitted. The entire casing is preferably surrounded by an insulating covering 44 to prevent the loss of heat during the carbon impregnation reaction.

The apparatus of my co-pending application having been operated and controlled to produce the requisite coating and/or impregnation of the oxide with carbon, the stream of cracked and partly decomposed hydrocarbon vapor, which has entrained therein the coated and/or impregnated ore, is discharged from the reaction chambers of the apparatus. A separation of the impregnated ore from the vapor can be effected by any suitable dust separating process, for example, by centrifugal separation, and the vapor then conducted to a condensing tower, where its heat may be given up to the incoming hydrocarbon or otherwise conserved, while the coated and impregnated ore, in its still heated condition, is conducted to the reduction chamber of suitable reducing apparatus.

Apparatus particularly adapted for handling finely divided ore is that described and illustrated in the co-pending application of James C. Hartley, Serial No. 338,560, filed June 3, 1940 and in the co-pending application of Herman A. Brassert and James C. Hartley, Serial No. 323,076, filed March 9, 1940, of which application the application Serial No. 338,560 is a continuation in part, in which the finely divided ore is maintained in a condition of substantially continuous agitation and progression while being exposed to reducing heat, the agitation and progression being effected by means of a heated fluid through which a substantial part of the reducing heat is supplied to the oxide to be reduced. In the case of the carbon impregnated ore, the heating and agitating fluid or gas may be a neutral non-oxidizing gas, or it may be a reducing gas, such as carbon monoxide or hydrogen or a mixture of carbon monoxide and hydrogen, depending somewhat upon the nature of the impurities that may still remain in the coated and impregnated ore.

The preheated hydrocarbon vapor with its entrained preheated ore passes in succession through the chambers 12 and 16 of the impregnating apparatus hereinabove described, in which apparatus it travels in succession through zones of relatively high velocity and reduced pressure and of relatively lower velocity and higher pressure and is thus subjected to marked turbulence resulting from these sudden changes of pressure and velocity and also from the action of the streamlined baffles 24 and 34, with incidental recirculation back through the venturis. After undergoing the thorough commingling and interaction in the chambers 12

and 16 the reformed hydrocarbon and impregnated ore enter the discharge pipe 42, the ore being now thoroughly impregnated and/or coated with carbon resulting from the decomposition of the hydrocarbon and the hydrocarbon having been reformed as a result of the catalytic action of the ore. The discharge pipe 42 is connected with a centrifugal separator 45 which may be of any usual construction in which by centrifugal action the carbon coated and impregnated ore is separated from the reformed hydrocarbon gases and/or vapors, the ore passing downwardly through the discharge pipe 46 into the reduction chamber 48 of reduction apparatus presently to be described and such as shown in the co-pending application of Herman A. Brassert and James C. Hartley, Serial No. 323,076, filed March 9, 1940, of which the application of James C. Hartley, Serial No. 338,560, filed June 3, 1940, is a continuation in part. The reformed hydrocarbon gas or vapor passes out through the discharge pipe 50 by which it may be conducted to any suitable condensing tower or fractionating apparatus as hereinabove suggested.

The finely divided ore which has been coated and impregnated with carbon in the reaction chamber hereinabove described and separated from the reformed hydrocarbon vapor or gas in the centrifugal apparatus 45 is delivered by the pipe or chute 46 upon the refractory hearth 52 which is perforate, the perforations 54 being all inclined forwardly in the same general direction as shown. The reaction chamber 48 may be enclosed by a wall 56 of heat-resisting material and in turn be located within a heating chamber 58 having a surrounding wall 60 of heat-resisting material, which, in turn, is surrounded by heat insulating material 62. Burners 64, located beneath the floor of the chamber 48 and supplied by a gas manifold 66, provide means for supplying external heat to the chamber 48 and also to the manifolds 68 which supply heating and agitating gases to the perforations or jet orifices 54. The heating and agitating gases for the orifice manifolds 68 are supplied to these manifolds through a longitudinal manifold 70. The manifold 70 is heated by the products of the reaction leaving the chamber 48 through the discharge pipe 72 and passing through a jacket 74 surrounding said manifold.

The gases introduced into the orifice manifolds 68 through the longitudinal manifold 70 are under pressure and as they pass up through the orifices 54 in the hearth 52 they effect an agitation and advancing movement of the ore 76 delivered to this hearth through the pipe 46 thus insuring a complete reduction. These gases, which in the case of a carbon impregnated ore need not contain any reducing constituents, are, of course, non-oxidizing, their purpose being to provide agitation, additional heat to raise the ore to the reduction temperature and advancing movement of the ore over the hearth into the discharge pipe 78. Any suitable non-oxidizing gas may be used for this purpose, but I prefer to use carbon monoxide since it will mix with the carbon monoxide formed as the product of the reduction in the chamber 48 and thus can readily be recovered in any suitable recovering or reforming apparatus.

It is important, of course, in the reduction of finely divided iron ores, at temperatures below the melting point of the iron, that the sponge

iron resulting from the reduction, which is very readily oxidizable, is catalytically quite active and, when produced at low temperatures, is pyrophoric, be protected against reoxidation until it is either converted into a finished product or reduced to a temperature at which it is not so readily oxidized. Sponge iron, produced at the temperatures preferable employed in the reduction of the oxide in accordance with the present process, that is, from 1400° F. up to 1800° F., does not usually show pyrophoric characteristics and it is therefore primarily essential to insure its protection against reoxidation.

This protection can be afforded either by maintaining the sponge iron, resulting from the reduction, in a protective non-oxidizing atmosphere until it is cooled below the temperature at which it is readily oxidizable or it may be handled in such a way that the heat still remaining in it at the end of the reduction operation may be conserved. Processes for converting the reduced sponge iron into finished products, in which processes at least part of the heat remaining in the iron at the end of the reduction step is utilized in the next step, are disclosed in the patent applications of Herman A. Brassert, for improvements in the Manufacture of metal products, Serial No. 316,717, filed Feb. 1, 1940; Serial No. 318,814, filed Feb. 14, 1940; and Serial No. 319,197, filed Feb. 16, 1940.

As hereinabove suggested, the hydrocarbon vapors, after having passed over the catalytically active oxide, will have one or more of their higher boiling point constituents decomposed to furnish the carbon for treating the oxide and this decomposition, and possibly some cracking without carbon deposition, will usually effect such a reformation of the higher boiling point constituents of the hydrocarbon as to produce a resultant hydrocarbon oil having a lower end boiling point. This hydrocarbon can be condensed in the manner hereinabove suggested and preferably in such manner that its contained heat will be utilized, as, for example, in preheating the hydrocarbon which has not yet been brought into reactive association with the ore.

From the foregoing description it will be seen that the process of the present invention in-

5 sures such an intimate association of a solid reducing agent with an oxide to be reduced that when the treated ore or oxide has been brought to the reducing temperature a quick and complete reduction will result.

What is claimed as new is:

1. That step in the reduction of metallic oxides capable of effecting catalytic decomposition and/or cracking of hydrocarbons under certain temperature conditions, which consists in entraining the metallic oxide in a stream of a hydrocarbon, which is in the vapor state and is heated to the temperature at which the metallic oxide will effect catalytic decomposition of at least some of the constituents of the hydrocarbon, said oxide being in a finely divided condition and also heated to the said hydrocarbon decomposition temperature, setting up turbulence in said stream and maintaining the oxide and the hydrocarbon vapor in the intimate association thus brought about until the particles of the oxide have received the desired deposit therein and thereon of carbon resulting from the catalytic decomposition thus brought about.

2. A process according to claim 1, in which the temperature maintained in the reaction zone is above the decomposition temperature of at least some of the constituents of the hydrocarbon but below the reduction temperature of the oxide.

3. A process according to claim 1, in which the hydrocarbon vapor is brought into a turbulent state by causing it to flow in a laterally confining, overall speed-determining conduit through successive zones of higher than average velocity and lower than average pressure and of lower than average velocity and higher than average pressure and in which the oxide, in a finely divided condition, is entrained in the stream of hydrocarbon vapor to partake of the turbulence therein thus created.

4. A process according to claim 1, in which a separation of the entrained treated oxide from the reformed hydrocarbon is effected without cooling and the treated oxide is then raised to and maintained at the reduction temperature until the oxide is reduced.

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