

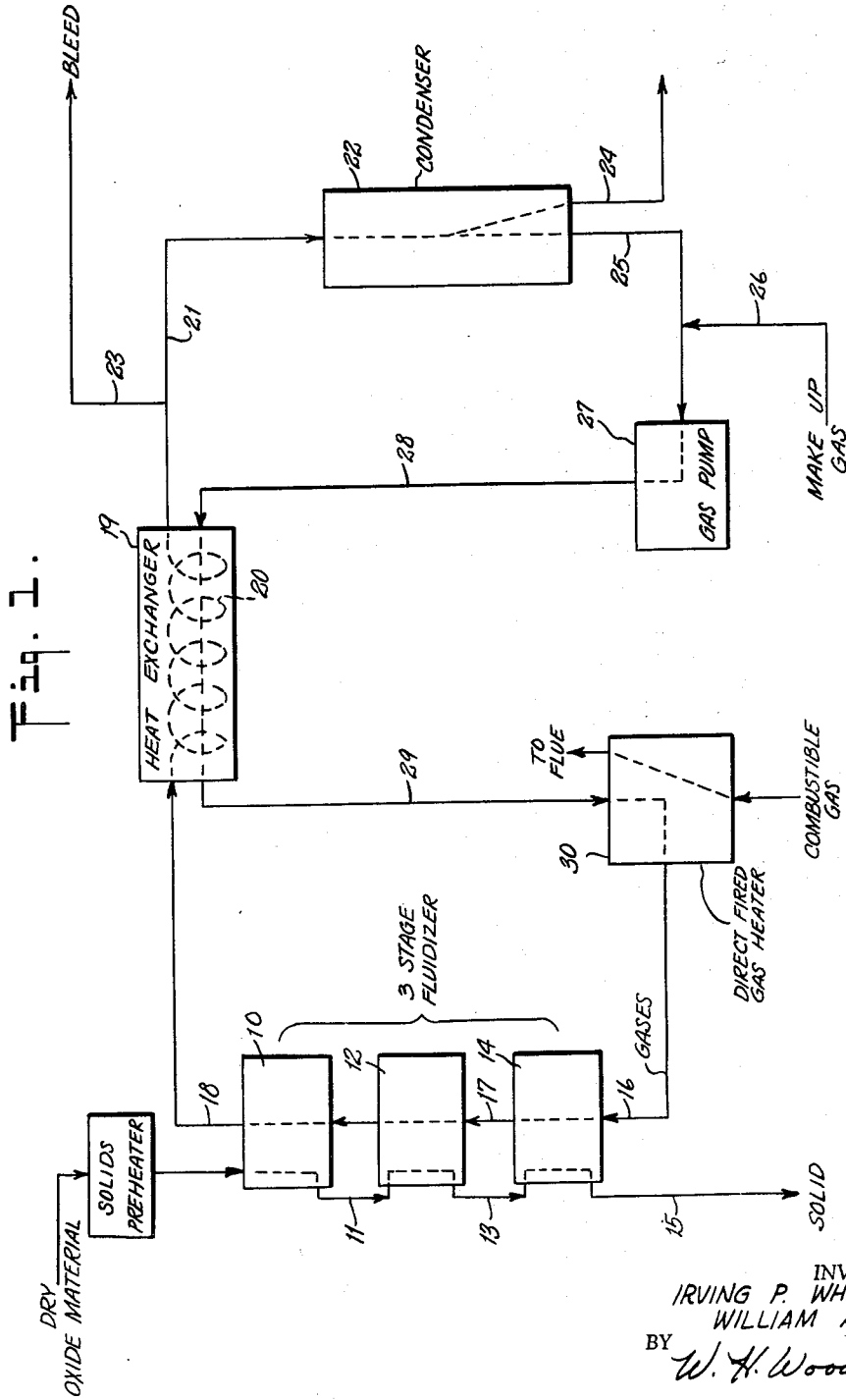
Aug. 2, 1960

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OF BEING ROLLED DIRECTLY TO SHEET FORM

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2 Sheets-Sheet 1



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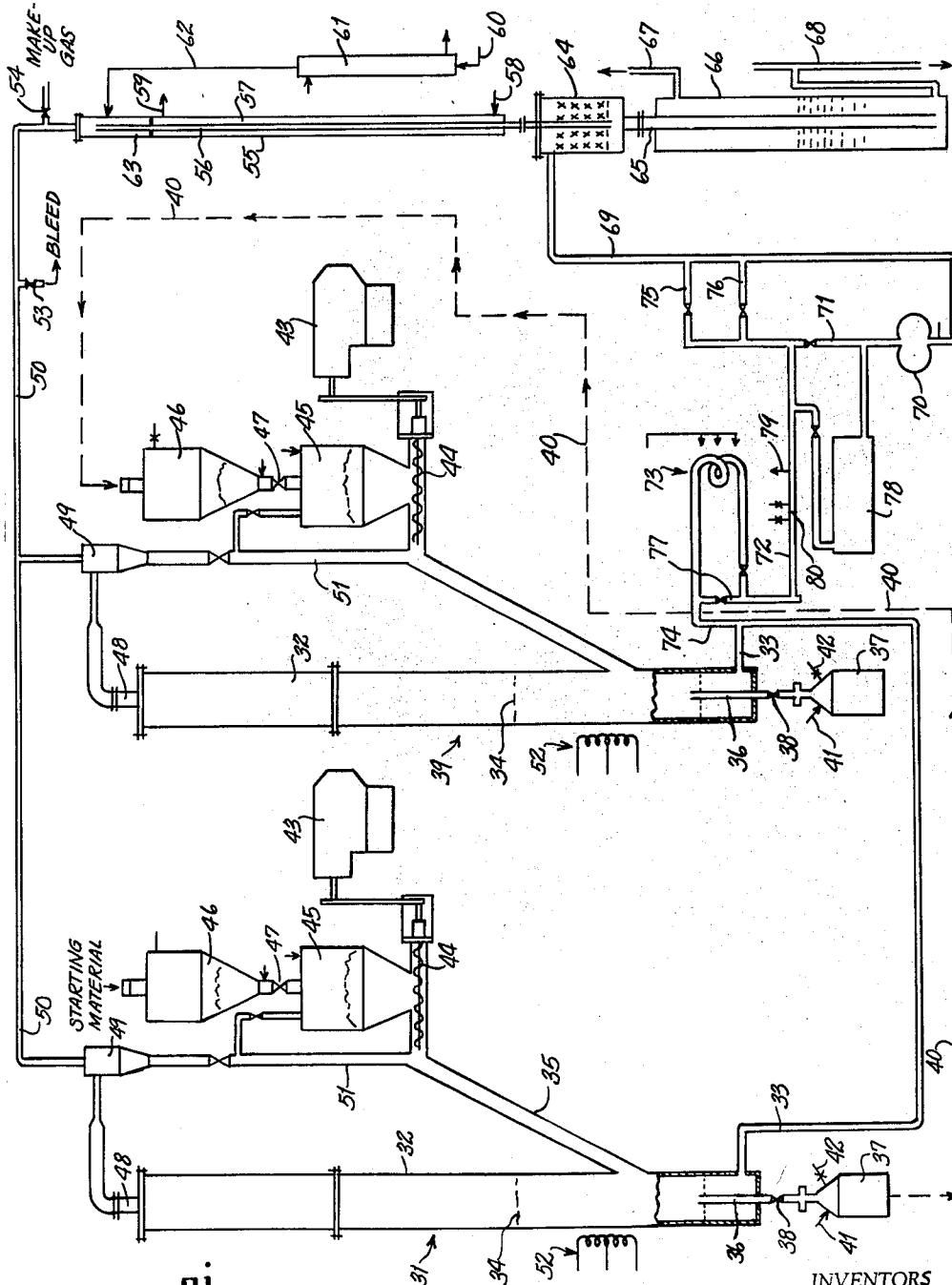


Fig. 2.

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PROCESS OF PREPARING IRON POWDER CAPABLE OF BEING ROLLED DIRECTLY TO SHEET FORM

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3 Claims. (Cl. 75—5)

The present invention relates to a process of preparing iron powder capable of being rolled directly to sheet form. More particularly, the invention relates to a practical, reasonably economic process by which iron powder of a type capable of being directly fabricated into sheets, for example, may be made by the reduction of iron-oxide material in a plural stage, fluidized bed-type apparatus.

It is recognized that the prior art has known for many years how to produce iron powder by reducing one or more of the oxides of iron; and further that, if the particular process be disregarded for the moment, iron powder capable of being rolled directly into sheet form has been produced by reduction processes. It is further recognized that fluidized bed-type reduction operations for iron powder have been known for some time and in some instances that these operations have been conducted on a plural-bed basis. There are, however, certain special requirements for iron powder which is capable of being rolled directly into sheets and which requirements, while having been complied with by certain different type operations, have not been generally considered attainable when operating on a fluidized bed basis and when the starting material may contain some impurities. In other words, the features of the present invention are believed to be novel in their entirety; although individually, the several features or steps may have been used respectively in other connections and/or for the making of materials which would not qualify in accordance with one or more of the requirements of the product of the present invention.

Among the requirements for the product of the present invention are that it have a hydrogen loss of not over 1½%. By this is meant that the loss in weight of a sample of the product when heated in pure hydrogen for one hour at a temperature of 2000° F. is not over 1½% of the starting weight. This is a usual requirement imposed by the commercial powder metallurgy industry upon metal powder, which this industry considers satisfactory. As a practical matter, it is usually desired that the hydrogen loss be considerably less than the limit here given.

The next requirement for powder in accordance with the present invention is that it have a content of acid-insolubles of not over about 1%; and further, that these acid-insolubles shall be in a particle size not over about 200-mesh. The reason for this last requirement is that larger particles of acid-insolubles, such as silica and/or alumina, when present in an iron powder which is rolled directly into sheet form, will cause a surface streak which will so impair the surface appearance of the sheet that the product will be considered commercially undesirable, if not wholly unsatisfactory.

The only time that the presence of acid-insolubles is practically a real problem is when the starting material is an ore. In such cases it is common to give the ore, if not of a magnetite type, a partial reducing roast so as to convert it to the form of magnetite (Fe₃O₄). The magnetite may then be separated from the gangue (most

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of the acid-insolubles) by magnetic separation, the efficiency of which may now be made quite high, particularly if the solid material is in relatively fine particle form. This separation and the reduction of the acid-insolubles to a desired minimum size is per se no part of the present invention, but is practically necessary in the handling of ores, whether they be in the form of magnetite initially or be converted to that form. The present invention starts with a body of iron oxide, including any one or more of the oxides of iron, and with a total content of acid-insolubles of not over about 1%, so that the total amount of these materials is in effect no problem from the point of view of the present invention.

What is a problem, however, is the particle size. As stated above, it is necessary that any acid-insolubles present shall be in a particle size of not over about 200-mesh. There is, of course, no real problem to get the particle size of all the original material down to 200-mesh. However, it is practically impossible to get the acid-insolubles down to a 200-mesh size without at the same time reducing all material present to about that size. This introduces another and very important difficulty, which is that while there are some processes of reduction of iron-oxide which can accommodate materials of 200-mesh and finer, yet the ordinary and known processes of fluid bed reduction normally call for much coarser material, or at least some of the material in much larger particle sizes. When all material is 200-mesh and finer, very substantial difficulties are introduced into the reduction thereof on a fluidized bed basis. It is to the solution of these difficulties that the present invention relates; and all the particular steps and limitations hereinafter set out are in effect required for the proper and commercially practicable solution of the difficulties introduced by the very fine material which must be used as the starting material.

One obvious way in which these difficulties might be attacked would be to sinter the material in some way or possibly to nodulize it; but in either event, such material would not be suitable for handling on a fluidized bed basis. The present invention, however, provides certain novel combinations of process steps and conditions, which while in some instances individually known or heretofore used, have not been collectively assembled into a single process for the handling of material which is not susceptible of fluidized bed reduction in any other way.

Summarizing the present invention, therefore, it comprises the preparation of powdered metallic iron capable of being rolled directly into sheet form without intermediate melting and having a hydrogen loss and content of acid-insolubles as aforesaid, and in which the acid-insolubles exist in a particle size of not over about 200-mesh, the process itself involving the plural stage (at least two stages) reduction of an iron oxide material by contacting it in each stage with a gaseous reducing agent, the active reduced constituents of which consist essentially of hydrogen (other reducing gases being found inappropriate in accordance with this invention). It is found necessary that the rate of gas flow through the fluidized bed of each of the stages shall be from about ½ to about 1½ feet per second and further, that the temperature conditions in each of the stages shall be within certain limits which, for all the stages except the last (as to the solid materials), is from about 900° to about 1200° F. and for the last stage from about 100° to about 1100° F. The material as finally reduced is pyrophoric, even when cooled under non-oxidizing conditions. Thus, the material (iron powder) must be protected from direct contact with the atmosphere until it is in some way (per se forming no part of this invention) converted to a form which is non-pyrophoric.

The process of the present invention is illustrated

diagrammatically in the accompanying drawings, in which:

Fig. 1 is a diagrammatic illustration of a cyclic process including a three-stage, fluidized bed reduction apparatus in which the solid materials being reduced pass successively from the first to the second to the third stage; while the reduced gases pass, in effect countercurrent to the solid materials, and from the third to the second to the first stage; and

Fig. 2 is a somewhat more detailed diagrammatic illustration, but with some parts broken away and in vertical section, of a two-stage process in which the gases are supplied in effect in parallel to the two-stages rather than successively from one to the other.

Referring first to the form of the invention shown in the very diagrammatic Fig. 1, it will be seen that the solid material, which is designated in the legend on the drawing as "Dry oxide material" is supplied as indicated by the arrow to a first stage reaction chamber 10 and thence is conveyed in an appropriate manner indicated by an arrow 11 to a second stage reaction chamber 12 through which the solid materials pass as indicated by the dotted lines. The solid materials from this second stage reaction chamber then flow in a suitable manner indicated by an arrow 13 to a third stage reaction chamber 14, from which they are eventually withdrawn by and to suitable means as indicated by an arrow 15.

There is also diagrammatically illustrated in Fig. 1 a suitable means for preheating the solid materials as supplied to the reaction chamber 10, which constitutes the apparatus for the first stage of the process. While it is possible and is within the purview of the present invention that the solid materials may be supplied to the reaction chamber 10 at substantially room temperature and heated up therein to the desired operating temperature in this first stage as hereinafter set up, yet it is generally preferred from a commercial point of view to preheat the solid materials to substantially the desired temperature prior to introducing these materials into the reaction chamber 10.

This preheating may be carried out in any suitable type of apparatus, many of which are known to the art, including, for example, such apparatus as gas fired preheaters through which the solids to be treated are conveyed in a substantially closed muffled-type passage by a screw conveyor, similar apparatus in which the heat is applied electrically by resistance coils wrapped around the muffle, as well as fluidizer equipment wherein the sole purpose is to preheat the solid materials by passing a neutral gas therethrough at a sufficiently high temperature and/or wherein the heat is supplied to the materials in a fluidizer equipment by a heated jacket arranged around this fluidizer. Other types of solid preheating equipment will occur to those skilled in the art as equivalents to those specifically mentioned and all are to be considered within the purview of this invention.

The starting material for the process may consist of any suitable oxide or mixture of the oxides of iron having a particle size of not larger than about 200-mesh and having a total content of acid-insolubles of not over about 1%. It is contemplated, for example, that this material may be suitably comminuted mill scale, wherein the problem of acid-insolubles is not present, as the material is a relatively pure iron oxide by-product from iron and/or steel manufacturing operations. It is also contemplated, for example, that iron ore could be used; except that under such circumstances, suitable concentration (presumably by magnetic separation) must first be carried on in a manner per se forming no part of this invention, in order that the total content of acid-insolubles shall be reduced down to the permitted limits, i.e. not over about 1%. However, irrespective of the source of the starting material, it will consist of one or more of the oxides of iron with not over about 1% acid-

insolubles and will be supplied in a suitable manner to the first stage reaction chamber 10.

The particular problem which must be discussed from the point of view of the present invention is to handle the necessarily very fine particle size material, inasmuch as the starting material must be all in a particle size of not over about 200-mesh in order that the acid-insolubles shall be in this small particle size. In conventional forms of fluidized bed apparatus as taught in the prior art, it was usual to use a solid material having a graded set of particle sizes up to, for example, 10-mesh or possibly as fine as 50- or 60-mesh as the coarsest material present. Under these circumstances, conventional types of fluidized bed equipment and conventional values of the several variables including temperatures, gas velocities, etc., can be used. It is found, however, that when quite fine material as contemplated with the present invention must be handled on a fluidized bed basis, special precautions must be taken, first with respect to gas velocities, which should be in the order of magnitude of about $\frac{1}{2}$ to about $1\frac{1}{2}$ feet per second.

It has also been found, according to the present invention, that the temperature range for operating with very fine material according to this invention must be kept down substantially below those temperature ranges which have been conventional in the fluidized bed reduction of iron in accordance with the prior art teachings. In the present instance the temperatures in all except the last stage, i.e. in the reaction chambers 10 and 12 according to the diagram shown in Fig. 1, must be within the broader limits of about 900° F. to about 1200° F. but preferably not over about 1100° F.

The reasons for these limits are first as to the lower limit, that at temperatures of below about 900° F. the reaction is so slow as to be commercially impracticable. On the other hand, at temperatures above about 1200° F., the tendency for the very fine particles to adhere or sinter together becomes so great that the proper operation of the fluidized bed with this fine material becomes impossible or at least impracticable. The preferred temperatures, even in the first stages, are about 1000 to 1100° F. and particularly about 1100° F., it being desired to keep away from the outermost limits hereinabove given for the same reasons for which those limits are set as aforesaid.

The temperature range in the last stage, where the material is very largely iron, must be kept within somewhat narrower limits, i.e. from about 1000° F. to about 1100° F. The reasons in this case are substantially the same as for the other stages, except that the tendency to sinter in the last stage is now much more severe than in the case of the relatively little reduced material present during the earlier stages.

Another reason for operating at temperatures not over about 1100° F. is that at least lower temperatures, the reduction reaction from magnetite (Fe_3O_4) to iron appears to be a direct reaction which apparently does not pass through the stage of FeO. It has been found that the reduction of FeO to Fe is per se quite difficult, at least in relation to the reduction of magnetite; so that if this intermediate stage can be avoided, the reduction proceeds with greater efficiency. It is desired to work in this favorable temperature range.

Again, in handling quite fine material as required in accordance with the present invention, it is necessary that the composition of the reducing gases shall be restricted to quite narrow limits. In this case it has been found that the only practical reducing gas is one wherein the reducing constituent consists essentially of hydrogen, as other known reducing gases are found to cause one or more difficulties which preclude their practical use. It is not intended by this statement to preclude the presence in the gases of one or more inert gases, for example nitrogen, or to put any limitation whatsoever upon the pro-

portion of inert gases on the one hand as against the active reducing gas, hydrogen, on the other.

There must be enough hydrogen to do the reducing which is required, both as to concentration with respect to water vapor, for example, and also from a stoichiometric point of view, as to the total amount of hydrogen which must be passed in contact with the material being reduced. It will be understood that as the starting material is basically one or more of the oxides of iron, there will be a proportionate amount of water vapor generated as the iron oxide is reduced. This water vapor is to a desired extent eliminated from the gases during the recycling thereof and incident to the rehabilitation of the gases which will be discussed hereinafter.

From another point of view, the presence of nitrogen or other inert gases is positively contemplated for use under some circumstances. It is contemplated that once the materials in any one stage have been brought up to a temperature desired for that stage, the maintenance of this temperature may be effected by the supplying of the necessary heat in the form of sensible heat in the gases supplied to and through this stage. It is further contemplated that, if desired, the heating up of solid materials in any one stage may be effected, while maintaining these materials in a fluidized condition, by passing an inert gas therethrough, such inert gas being, for example, nitrogen. Under these circumstances it is contemplated that the heat may be supplied to bring the materials and the environment to the temperature as sensible heat in the inert gas thus used. The particular connections and arrangements for using an inert gas for the heating up of the material in the several stages is not shown in the accompanying drawings. Such an expedient is, however, contemplated as a part of the operation according to the present invention, it being understood that suitable means (not shown) will be provided in conjunction with an actual operating apparatus to permit the carrying out of these desired operations.

It is further contemplated that the solid material being treated may be in effect in a continuous operation or in effect in a batch operation. By this is meant that, from a continuous point of view, it is contemplated that starting materials may be substantially continuously supplied at a relatively slow rate to the first stage reaction chamber 10 and may be substantially continuously withdrawn therefrom, also at a very slow rate, through the passages or means indicated at 11, to the second stage reaction chamber 12, etc. Alternatively, it is contemplated, for example, that the materials in a sufficient amount to provide a suitable charge for the first stage reaction chamber 10 may be supplied thereto and then maintained therein in a fluidized condition for a desired time prior to withdrawing them, either continuously or intermittently, from this stage for supply to the next stage reaction chamber 12, etc. In this way the "holdup" time for each stage may be adjustably predetermined at will.

It is normally intended that the solid materials shall be supplied directly from one stage to the next, so as to retain therein the sensible heat and avoid the necessity for heating these materials up between stages. On the other hand, it is contemplated that if the operation should be such that it is more desirable, the materials from an earlier stage could be taken to a suitable intermediate storage point and either maintained hot or allowed to cool and then reheated as necessary prior to their introduction to the next stage.

From the point of view of the gases, and considering the form of the invention diagrammatically shown in Fig. 1, the fresh gases are supplied as indicated by an arrow 16 to the last stage, shown as the reaction chamber 14, and thence pass through that stage as indicated by the dotted line; then pass from that stage to the second stage as indicated by the full line arrow 17, and so on to the exit from the first stage, from which the gases pass through suitable passages indicated by the full

line arrow 18. In accordance with this form of the invention there is no rehabilitation of the gases between stages which will in any way affect the composition of the gases; although it is contemplated that if desired, some suitable temperature control, including either the heating or the cooling of the gases between stages, may be carried on so as to maintain temperature conditions in the several stages at the desired values respectively. Such temperature conditioning is not represented on the drawings, but could, for example, involve the interposition of a gas heating device midway of the passage indicated by the arrow 17.

Following the passage of the gases out of the first stage as indicated by the solid line arrow 18, these gases are passed through a suitable recycling system and rehabilitated so as to be reusable. This rehabilitation involves several essential elements or process steps. A first of these, which is not illustrated in the diagram of Fig. 1, is to separate from the gases a very large part, if not all, of the solid materials which are entrained therein. It will be understood that, due to the very small particle size of the solid material being handled in accordance with the present invention, this problem of entrainment is quite serious and must be taken into account. The actual equipment for handling it will be described in more detail in connection with Fig. 2, but must be understood to be present also in the form shown in Fig. 1. In the usual situation, a cyclone-type separator will be sufficient to remove a large part of the entrained solid material, which solid material is normally returned to the stage from which it passed by entrainment in the gases. Thus, in the form of Fig. 1 it will be understood that suitable separating means are provided in conjunction with the equipment of each of the stages comprised by the reaction chambers 10, 12 and 14, and that the solid material so separated from the gases leaving these stages is returned to the respective stage from which it came.

The next operations in conjunction with the rehabilitation of the gases may take place in any of several orders and involve three essential steps including (a) bleeding out of the recirculation system as herein set out a selected part of the gases, so as to prevent building up in the gases being recirculated an undesired concentration of inert gases, such as nitrogen; (b) adding to the gases being recirculated a desired amount of fresh hydrogen-containing gases, so as to build up the concentration of hydrogen therein to a desired amount; and (c) condensing out of the gases a selected amount or proportion of the water vapor therein, so as to control the amount of water vapor in the gases as recycled. In addition to this there is always required the reheating of the rehabilitated gases to a temperature desired for the reintroduction thereof into the reaction chambers, which in the case of the form shown in Fig. 1 comprises first the chamber 14, which is the last reducing stage.

The reheating operation and the cooling of the gases is in part jointly accompanied by the provision of a heat exchanger or interchanger 19, through which the gases exhausted through the passages represented by the full line arrow 18 from the first stage reaction chamber 10 are passed as indicated by the looped dotted lines 20. Thus, some of the heat thereof is used for reheating gas en route back to the reducing zones, i.e. the reaction chambers 10, 12 and 14.

As shown in Fig. 1, gases pass from the heat exchanger 19 through a duct system indicated by the solid line 21 to a condenser 22. Part way along this path is indicated a bleed passage 23 for removing from the gases some selected part thereof, so that if the makeup gases herein-after described contain some inert constituent, such constituent will not be allowed to build up to an undesired high value of concentration.

As stated before, another of the essential features in rehabilitating the gas is to remove therefrom a selected

part of its water vapor content. This most conveniently done by providing a condenser, indicated diagrammatically at 22, through which the gases pass and in which the temperature is reduced so as to control the residual water vapor content, which in turn is controlled by the exit temperature thereof. As shown, water removed from the gases by condensation may be discharged through a line 24, while gases pass out from the condenser through a duct system indicated by a line 25.

Fresh hydrogen-containing gases, sometimes known as make-up gases, are shown supplied to the gases being recycled through a branch duct indicated by a line 26 joining the line 25. It will be understood that the gases being supplied must contain hydrogen and usually have a higher hydrogen concentration than that required for the gases introduced into the reducing stages. On the other hand, the fresh gases may also contain some inert gas or gases. Thus, for example, a commercially produced gas including about 95% hydrogen and 5% nitrogen (neglecting the water vapor content at the moment) is satisfactory as a make-up gas.

At some point in the recirculation system it is necessary to provide a gas pump or equivalent means in order to assure the positive flow of gases at a desired velocity. Such a means is indicated diagrammatically at 27, this pump receiving mixed gases from the lines 25 and 26 and forcing them through a duct system indicated by a line 28, first through the heat exchanger 19 and then through another duct system indicated by a line 29 to a gas heating apparatus 30 indicated as a direct-fired gas heater. It will be understood that the apparatus 30 may take any desired form, the only requisite being that it will serve to heat the gases to a desired and controlled extent. As diagrammatically shown, the apparatus 30 is in the form of a gas heater through which the gases pass in a series of pipes or ducts which are externally heated by combustion gases, there being a suitable supply of combustible gas thereto and a suitable flue being provided in a usual manner. Any means usable for heating gases up to a desired and controllable temperature may be employed as the apparatus 30.

The gases from the apparatus 30 pass thence through a duct system indicated generally by the line 16 to and through the several stages of the reducing apparatus, completing the cycle.

Due to the fact that iron in fine powder form and reduced as aforesaid is pyrophoric, even after cooling under non-oxidizing conditions, it must be kept out of contact with the air or other oxidizing gases. It will be understood that such provisions are made in a manner not indicated in Fig. 1.

The iron powder (product of the present process) may then be employed in any way desired, all of which forms per se no part of the present invention. One way, however, in which this product may be used advantageously is for rolling directly into sheet form. For this purpose the iron powder is maintained out of contact with the air until it has been compacted by the rolling operation to a point such that the compacted article is no longer pyrophoric. This operation, however, is merely one use for which the product of the present invention is adaptable and is not to be considered as a necessary limitation upon the use of this product. The present invention concerns itself rather with the preparation of a product which has characteristics such as to enable it to be used for this particular purpose as well as for others, the purpose being stated solely to impose certain limitations as herein set out on the characteristics of the product.

Referring now to the form of the invention shown in Fig. 2, there is illustrated a variant of the process of Fig. 1 and yet one in which individual steps are essentially similar to those previously described. In this case, however, the apparatus is shown somewhat more in detail. The form of Fig. 2 differs from that of Fig. 1 principally in that there is a single system for rehabilitat-

ing the gases; but the gases, instead of being passed sequentially through the several stages, are passed in effect in parallel through these stages, so that the fresh gas from the rehabilitation system is divided in this instance into two portions and one portion passed through each of the two reduction stages provided. The gas exhausted from each of the two stages is combined together and then passed through the rehabilitation system.

A further difference is that, in the form of the invention of Fig. 2, only two stages are provided, rather than three, as shown in the form of Fig. 1. It is found that two is enough for certain purposes; except, however, that three or more may be used if desired.

Referring now in detail to Fig. 2 and in particular to the first stage apparatus generally indicated at 31, there is shown a fluid bed reaction chamber or reduction apparatus comprising a substantially vertical column or cylindrical container 32, into a lower portion of which gases are passed from a pipe or conduit 33, so as to flow upwardly through the solid material, which is thereby maintained in a fluidized or turbulent condition substantially up to a level as indicated, for example at 34. Much has been written about the operation and construction of fluidized bed apparatus. The present invention does not purport to provide anything novel in the way of such apparatus or in the physical operation thereof, but contemplates the employment of known or conventional apparatus operating in a known manner, except as herein specifically set out. The theory of operation of a fluidized bed and the particular construction of the apparatus used therein will, therefore, not be described in further detail.

Solid materials are supplied to the fluidized bed in the column 32 through an inclined duct 35 and are exhausted therefrom through an inclined duct 36 leading to a closed receptacle 37 and provided with a suitable valve 38. It will be understood that the receptacle 37 may be sealed and then detached from the duct 36 once the valve 38 is closed; and that it may be conveyed while still sealed, to some other point for transporting the contents thereof to such other point. This is the process as generally indicated in Fig. 2 for transporting the material passing out of the first stage 31, so as to introduce it into the second stage apparatus here generally indicated at 39. A broken line 40 is shown on the drawings to convey the idea that the product of the first stage is intended to be conveyed over and introduced into the second stage, while preventing contact thereof with the air, which would tend to re-oxidize some of the reduced iron. For this purpose the receptacle 37 may be provided with suitable means indicated by an arrow 41 and a valved duct 42 for passing a non-oxidizing gas thereinto and exhausting it therefrom, so as to maintain the solid materials therein under non-oxidizing conditions.

It will be understood that the apparatus used for the first and second stages as shown in Fig. 2 may be constructed in the same manner, so that in the present drawings, the parts are given the same reference characters to the extent that they are duplicated in the two stages.

In each stage of the apparatus shown in Fig. 2 there is provided feeding means for supplying the solid material thereto at a variable and controllable rate, such means including a motor and variable speed drive combination generally indicated at 43, which is suitably connected to drive a worm or other equivalent feeding means indicated at 44, which in turn controls the rate of feed of solid material from a supply hopper 45 to the inclined duct 35. The supply hopper 45 may in turn be fed by gravity from another supply hopper 46, having a valved passage 47 through which the material may flow to the hopper 45. The valves are provided so that if it is desired to operate the fluidized bed in the apparatus 31 at some pressure other than substantially atmospheric, such superior or sub-atmospheric pressure may be maintained without difficulty incident to the feeding operation.

Means are also provided as generally indicated in

Fig. 2 in conjunction with each stage for stripping from the gases passing out of each stage a large part, if not all, of the entrained solid material. For this purpose, and as shown in the drawings, the gases passing out of the top of the column 32 are conducted through a passage 48 to a cyclone separator 49, in which they are separated from most of the entrained solids, the gases passing from the cyclone separator 49 through a duct 50 to the rehabilitation means hereinafter described and the solids passing downwardly from the cyclone separator 49 through a valved passage 51 to the inclined duct 35. Thus the entrained solids from each stage are, to a major extent at least, separated from the gases passing out at that stage and returned to the same stage.

In this form of the invention, and as diagrammatically illustrated, an external heating means 52 is provided for each column 32, which means may be used if desired to augment or in lieu of the heat supplied as sensible heat in the gases entering each stage. This is particularly useful in starting up the device and in bringing the initial charge of solid material up to the desired operating temperature; it being usually preferred, once this system is brought up to temperature, that the desired temperatures be maintained by introducing the necessary amount of heat as sensible heat in the gases entering each stage.

In Fig. 2, the gas rehabilitation system is shown in somewhat greater detail than that in Fig. 1. As shown in this figure, the gases from both stages are supplied to the pipe 50, which is provided with a branch pipe 53 having a suitable valve therein for controlling the bleed of gases out of the system as may be necessary and as described in conjunction with the passage 23 of Fig. 1.

In this form of the invention the next step in the rehabilitation of the gases is to introduce make-up gas, which is done through a valved pipe 54 leading from a suitable source of such make-up gas. Again, the constituents and reasons for the make-up gas are as previously described. It will be noted here, however, that the make-up gas is supplied to the recirculation system in advance of the condenser, so that all the gas, including that portion supplied as the make-up gas, will be brought to a desired condition of humidity or water vapor content, wholly apart from the proportions of make-up gas used.

The gases are then supplied to a condenser 55, which is diagrammatically illustrated as a falling-film-type condenser. In the condenser 55 the gases are conducted downwardly through a substantially vertically extending tube 56, which is surrounded by a jacket 57 for cooling medium. The cooling medium is supplied to and passes away from the jacket 57 through the passages 58 and 59, respectively. Water is supplied from a suitable source through a pipe indicated by an arrow 60 and first passes through a suitable temperature controlling chamber 61, in the nature of a heat interchanger, so as to control the temperature thereof. This water then passes through a pipe 62 to the upper end of the condenser 55 and collects in the annular space 63 around the upper end portion of the tube 56. This water then overflows and passes down the inner walls of the tube 56 in contact with the gases flowing downwardly therethrough. This results in a very high coefficient of heat transfer between the gases and the condenser walls, and also in controlling the water vapor content of the gases within very narrow limits. It further serves to wash out of the gases and carry along to a suitable disposal point any fine particles of solid materials which were not previously removed from the gases and might otherwise collect in and clog up the condenser or some other part of the system in any protracted period of operation.

The tube 56 from the condenser has an extension at its lower end leading the gases to the lower end portion of a mist separator 64. The gases flow from the lower portion of this mist separator through a perforated sup-

port and thence through suitable materials as would be used in a scrubbing tower to assist in condensing out of the gases any entrained mist particles. The water flowing through from the pipe 60 via the pipe 62 and thence downwardly through the tube 56, and also the condensate (water) which is separated from the gases by the condenser move downwardly through a pipe 65 from the mist separator 64 to a seal leg 66 which is used to separate this water from any entrained solid material which has been carried along therewith, while preventing outflow of gases to the atmosphere. A gas vent 67 may be provided in connection with the upper end of the seal leg 66 for occasionally venting small amounts of gases therefrom; while the lower end thereof may be connected through an overflow drain device 68 through which water may be removed from the system.

The gases being recirculated pass from the mist separator 64 through a pipe 69 and may then pass directly through to a gas pump 70 and thence be forced into a pipe 71 and thence through a pipe 72 and a heater 73 to a pipe 74. As shown, several valved shunt passages are provided, including passages 75 and 76, each provided with a valve and each arranged in shunt of the pump 70 between the pipe 69 on the one hand and the pipes 71-72 on the other. There is also provided a shunt passage 77 by-passing the heater 73, this pipe and the pipe through the heater both being provided with suitable valves, so as to control the amount of gases passing through the heater and the complementary amount passing through the shunt passage 77.

It may sometimes be desirable to use the gas rehabilitation system of Fig. 2 with a single operating stage on a batch basis and with circulating gases used to control the cooling of solid materials, while continuing to maintain these materials in a fluidized bed or turbulent condition. Under these conditions it may be desired not only to by-pass the heater 73 altogether, but also to cool the gases positively. For this reason there may be provided a cooling means 78 through which the gases may be diverted between the pipes 71 and 72, this cooling means being arranged in a valved shunt passage as shown.

In addition, for facility in operation, an additional bleed out point may be provided at 79 and a restricted orifice interposed at 80 into the pipe 72 with provisions on each side thereof for determining the static pressures and thus the pressure drop across the orifice, so as to measure the gas flow. Inasmuch as these means are quite conventional, they will not be further described in detail.

As stated above, there is shown in Fig. 2 a single gas rehabilitation system connected in parallel to a two-stage reducing apparatus. It is contemplated that, if desired, one rehabilitation system for gas as shown in Fig. 2, for example, could be used for each of two or more stages of reducing equipment so that the gas temperature and composition for each stage could be independently predetermined to establish predetermined desired conditions in each stage independent of the other. This alternative is believed to be so obvious from the drawing and this description that further particular illustration is unnecessary.

The process of the present invention is further illustrated in the following examples:

Example I

In this example the raw material consisted of Adirondack ore, which was substantially all natural magnetite except that it was initially admixed with gangue. The ore was concentrated to a high degree by comminution and magnetic separation, so that the material as supplied to the present process analyzed 71.2% iron and 0.6% acid-insolubles. This material was concentrated to a particle size substantially all below 200-mesh and included 57% of minus 325-mesh. The material was supplied to the first stage reactor of a two-stage process

at the rate of 13 lbs. per hour, this amount of material being fed at the beginning of each hour of operation. The product was removed at the end of each hour, leaving about 100 lbs of material substantially continuously in the reactor, which was substantially as shown in Fig. 2 for the fluid bed reaction chamber 31. The fines recycled averaged as aforesaid about 5 lbs. per hour. At the end of the first stage operation, about 5 lbs. of fines were additionally recovered from the seal leg trap, shown at 66 in Fig. 2. The product of the first stage was about 74% reduced and contained 54% fines (i.e., minus 325-mesh). The bed temperature in this first stage was maintained in the range of 980° F. to 1050° F. The reducing gas entered the reactor at 1380° F. and passed through the bed at a velocity of 0.9 feet per second. The reactor walls were maintained at a temperature of about 1100° F. by an external heater as shown diagrammatically at 52 in Fig. 2; except that during the periods when solid materials were being fed to the reactor, the wall temperature was raised to about 1300° F. A small build-up of solid material was observed around the gas inlet at the end of the run, indicating some sintering at this point. The average hold-up time for the material in this first stage was about 10.5 hours.

The product of the first stage operation aforesaid was used as the feed for a second stage operation, into which it was supplied at the rate of 19 lbs. per hour, again maintaining a 100-lb. bed. The temperature of the bed in this case was maintained at about 1050° F. The gas used in this test as in the first stage operation aforesaid was 100% hydrogen, and the gas velocity in the second stage was 0.85 feet per second. About 4 lbs. per hour of fines were separated from the outgoing gases and returned during the second stage operation. The final product was about 96% reduced (equivalent to a hydrogen loss of 1.1%) and contained 52.4% fines (minus 325-mesh material). In the second stage the inlet gas temperature was maintained at about 1400° F. and the reactor walls were maintained at about 1200° F. At the end of this second stage run, 6 lbs. of fines were found to have been trapped in the seal leg shown at 66 in Fig. 2. The average hold-up time for the second stage run was 6 hours. This hold-up time was set so as to secure to desired proportionate degree of reduction and so as to reduce the hydrogen loss of the product to a desired low value.

Similar runs were made on a batch basis using the same type of raw material and with gas inlet temperatures up to 1570° F. It was found that the higher gas inlet temperatures caused sintering adjacent to the gas inlet only, so that in one instance a 4 inch plug of sintered iron powder had to be removed from the gas inlet after the run. Batch-type runs were also made at average temperatures of 900°, 1000° and 1100° F. in each instance in a manner similar to that above described. It was found that operations at about 1100° F. were generally to be preferred, as the reduction was faster and the rate of sintering not unduly high.

Example II

In this example the same type raw material was used for the process as in Example I, the starting material analyzing 71.2% iron and 0.6% acid-insolubles, the remainder being oxygen combined with iron. This starting material was reduced in two stages. In the first stage, the material was supplied at the rate of about 15 lbs. per hour and a 100-lb. bed maintained. The gas used as make-up gas in both stages in this test contained 95% hydrogen and 5% nitrogen. The temperature in the first stage was maintained at about 1075° F. About 20% of the feed was recovered in a cyclone separator associated with the first stage apparatus and returned to this stage. In addition, 3.6% of the feed was recovered in the seal trap associated with the first stage, there being

a separate gas rehabilitation system, each generally similar to that shown in Fig. 2, associated with each reducing stage apparatus respectively for this test. The product of the first stage showed a 73% reduction, which was equivalent to a 7.0% hydrogen loss. This product contained 33% fines (size range under 325-mesh). The product of the first stage was supplied as feed material to the second stage wherein the temperature of the bed was maintained at about 1000° F.

The operation in the second stage was substantially the same as in the first stage. About 8% of the solid material supplied to the second stage was separated from the gases leaving that stage in the associated cyclone separator and returned to this second stage. The second stage operations were continued until the final product was sufficiently reduced, this product having a hydrogen loss of 0.7% (equivalent to 98% reduction) and containing 29% fines. The average hold-up time in the second stage was 8.5 hours. There was no perceptible sintered material adhering to the walls of the apparatus used for the second stage reduction.

The products of both the runs in Examples I and II were of a character and quality requisite for direct rolling into sheet form as hereinabove set forth.

Example III

The process substantially as described above with respect to Fig. 1 was practiced upon a dry ore having an initial analysis (after suitable concentration as hereinabove described): iron—71.90%; oxygen (as oxide)—27.65%; acid insolubles—0.27%; silica—0.17%; carbon—0.01%. This ore was first preheated substantially to the operating temperature for the first stage as aforesaid, i.e. about 1000° F. The solid material passing from the first stage to the second stage, after about 5 hours' holdup time in the first stage, had a 13.6% hydrogen loss. This material had a hold-up time in the second stage of about 5 hours, and as passed from the second stage to the third stage, had a 3.0% hydrogen loss. The solid material leaving the third stage, in which there was also about 5 hours hold-up time, had a 0.6% hydrogen loss and had the following general analysis: iron—98.47%; oxygen—0.92%; acid insolubles—0.36%; silica—0.24%; carbon—0.01%.

The gases were passed through the several stages generally countercurrent to the flow of solid material there-through, so that the gas was supplied to the third stage at a temperature of 1180° F. and as so supplied had a composition as follows:

	Percent	S.c.f.
Hydrogen.....	92.5	10,800
Water vapor.....	2.5	292
Nitrogen.....	5.0	584

In the above tabulation, "s.c.f." stands for "standard cubic feet" and is intended to mean the cubic feet of the respective gas, when reduced by calculation to standard conditions of temperature and pressure. The data is given in this way for simplification of comparable data. The actual pressure in the third stage was about 7.5 p.s.i.g. (lbs. per square inch gauge). The pressure in the second stage was about 5.6 p.s.i.g. and in the first stage, about 2.5 p.s.i.g. The gases leaving the first stage had a temperature of only 520° F., which was considered unreasonably low for commercial operation, but was found to have been caused by lack of adequate insulation about the first stage apparatus and that portion of the gas line therefrom to the point at which the gas temperature was measured.

The gas composition leaving the first stage and en route to the gas rehabilitation system was as follows:

	Percent	S.c.f.
Hydrogen.....	86.7	10,115
Water vapor.....	8.3	977
Nitrogen.....	5.0	584

In this test, no heat exchanger corresponding to that shown at 19 in Fig. 1 was used, but the apparatus otherwise was as described for Fig. 1.

Tracing the course of the gases from the first stage to and through the rehabilitation system, the first change in gas composition was effected by bleeding out from the circulating gases a portion thereof made up as follows:

	S.c.f.
Hydrogen	146
Water vapor	14
Nitrogen	8
Total	168

These gases next passed through a condenser corresponding to that shown at 22 in Fig. 1, which removed an amount of water equivalent to 671 s.c.f. The gas passing out of the condenser was then augmented by make-up gas comprising hydrogen—831 s.c.f. and nitrogen—8 s.c.f., which was sufficient to make up the initial gas composition given above. The gases were then passed successively through a gas pump and a direct-fired gas heater and thence to the third stage of the reduction apparatus. The ore used in this example was —200 mesh and the process effected a 97.5% reduction thereof, which is considered to be satisfactory commercial operation.

Example IV

This example constituted substantially a repetition of the process set out in detail as to Example III with the exceptions, however, that in this example, only two reduction stages were employed. The hold-up time in each of these stages was increased from about 5 to about 7½ hours to compensate for the reduction in the number of stages. In this case, the total gas pressure in the second stage was 5.0 p.s.i.g., while that in the first stage was 2.5 p.s.i.g. The solid materials passing from the first to the second stage had about a 6.7% hydrogen loss and were about 74.6% reduced. With these exceptions, substantially the same conditions were established and maintained as in Example III.

While but a relatively few examples of the process have been given, and only two forms of apparatus have been more or less generally described, further modifications and equivalents of the subject matter herein described will occur to those skilled in the art from the foregoing description. We do not wish to be limited, therefore, except by the scope of the appended claims, which are to be construed validly as broadly as the state of the prior art permits.

What is claimed is:

1. The process of preparing powdered metallic iron capable of being rolled directly to sheet form and having a hydrogen loss of not over about 1½% and a content of acid-insolubles of not over about 1%, and in which the acid-insolubles exist in a particle size of not over about 200 mesh, said process starting with an iron oxide material having not over about 1% acid-insolubles; said process comprising the steps of comminuting all said starting material to a particle size of not over about 200 mesh; reducing said starting material in at least two reducing stages by contacting it in each stage and as hereinafter stated with a gaseous reducing agent, the active reducing constituent of which consists essentially of hydrogen and which contains not less than about 2.7 parts by volume of water vapor for each 100 parts by volume of hydrogen, maintaining the solid material in each of said stages in a fluidized condition by moving said gaseous reducing agent upwardly there-through, maintaining the velocity of gas travel through the fluidized bed of each of said stages from about ½ to about 1½ feet per second, maintaining the gaseous pressure in the last of said stages at not over about 7½ pounds per square inch gauge and in the first of said stages at not over about 2½ pounds per square inch gauge, maintaining the temperature in the first and all but the last stage (from the point of view of the solid material) in the range of about 900° F. to about 1200° F. and in the last stage, from about 1000° F. to about 1100° F.; and retaining the solid materials in the last of said stages until these materials are substantially completely reduced, so that the hydrogen loss thereof is not over about 1½%.

2. The process in accordance with claim 1, in which the solid materials are supplied to a first of said stages, and therefrom through each stage provided to a last of said stages, and the reduced solid material is withdrawn from said last of said stages; in which said gaseous reducing agent is supplied to said last of said stages, and is conducted thence through each stage provided to said first of said stages substantially countercurrent to the flow of said solid material; and comprising the additional steps of exhausting the gases from said first of said stages, then rehabilitating such gases to bring them to the composition and to the physical status of the gases supplied to the last of said stages, and then recycling the rehabilitated gases to said last of said stages.

3. The process in accordance with claim 1, comprising the additional steps of rehabilitating the gases exhausted from each of said stages to bring them to the composition and to the physical status of the gases supplied to said stages respectively, and recycling the rehabilitated gases to each of said stages.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,947,620

August 2, 1960

Irving P. Whitehouse et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, lines 57 and 58, for "acid-solubles" read
-- acid-insolubles --; column 2, line 64, for "1000"
read -- 1000⁰ --.

Signed and sealed this 31st day of January 1961.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents

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