United States Patent Office

2,950,955

Patented Aug. 30, 1960

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2,950,955

PROCESS FOR THE PREPARATION OF FINELY DIVIDED FERROMAGNETIC FERRIC OXIDE

Ernst Wagner, Rheinfelden, Baden, Germany, assignor to Deutsche Gold- und Silber-Scheideanstalt, Frankfurt am Main, Germany, a corporation of Germany

No Drawing. Filed Dec. 10, 1957, Ser. No. 701,708

Claims priority, application Germany Dec. 31, 1956

6 Claims. (Cl. 23—200)

The invention relates to a process for the direct production of finely divided ferromagnetic ferric oxide from ferric halides in the vapor phase.

It is known that like other oxides ferric oxide can be obtained by hydrolysis of the corresponding halide in a hydrogen-oxygen flame. In this process in general an excess of oxygen is used and the ferric oxide obtained is paramagnetic. For obtaining ferric oxide, iron pentacarbonyl has also been already used as the starting material and this was burned alone or together with other combustible substances. The preparation of magnetic ferric oxide has also already been described by processing iron carbonyl compounds with a deficit of oxygen, relative to the composition of ferric oxides.

It has now been found that finely divided ferromagnetic ferric oxide can be obtained directly in a simple way in the gas phase if volatile ferric halides are converted by hydrolysis within a flame of water-forming gases and in connection with this certain critical quantitative relationships with reference to the water-forming gases are maintained. According to the invention, the oxygen for the flame is proportioned so that the water formed is completely sufficient for practical purposes for the hydrolysis of the volatile ferric halide into an oxide of trivalent iron, while the hydrogen is applied in excess, referred to the formation of water. The ferric oxide, obtained according to the process of the invention, in contrast to the products of the processes previously known, is ferromagnetic even for almost stoichiometric composition, referred to Fe_2O_3. Because of its finely divided nature it is pre-eminently suitable as magnetogram-carrier, further for the preparation of magnetic solid solutions by pressing or also as agent for nondestructive testing of industrial materials. Likewise, of course, due to its extremely finely divided state and its activity, it can also be incorporated for purposes of which the utilization of the magnetic properties is not itself or not primarily the object, and it can serve, for example, as filler or also as pigment or polishing agent.

The process according to the application is not limited in the selection of water-forming gases for the flame to pure oxygen or pure hydrogen, although the latter is, however, preferably used, rather the production of the flame can take place through the utilization of hydrogen-containing and hydrogen-forming gases or gas mixtures such as illuminating gas, methane or the like, while air can be used advantageously as oxygen-carrier.

According to a particularly preferred form of procedure of the process according to the invention, the water-forming gases are mixed homogeneously together with the volatile ferric halides before bringing them to the flame, whereupon the reactive mixture is expediently led to the flame in laminar flow. In this form of procedure, the flame burns "autark" (self-sufficiently) in relation to all components required for the formation of Fe_2O_3 by hydrolysis, so that there is no dependence on the uncontrolled entrance of oxygen from the environment of the flame. Here it is important to make sure that the rate of outflow of the gas mixture from the burner opening is a multiple of its rate of flame propagation, and that, for example, by means of mechanical stripping or by flush gases, flowing past the burner mouth in a thin layer, the burner is protected from the deposition of a tuft, consisting of finely divided oxide, that causes clogging or that could disturb the uniform course of the reaction. Products obtained in this way are distinguished in particular by a largely uniform particle size, that is by a narrow band of granular size division and by uniform development of the surface of the individual primary particles. This depends on the uniform and homogeneous distribution of the various reaction components practically in the total flame volume, by which the same reaction conditions are created for each flame element. In connection with this, disturbances of the homogeneous formation of the flame, for example by turbulences, vortices or the like, are undesirable, therefore it is advantageous to lead the gaseous or vaporous initial mixture on the way to the flame and into it largely in a laminar way.

For the preparation of especially high grade products, for which a restoration of the surface is to be prevented as much as possible with reference to the maintenance of disordered places of the lattice and a granular growth, it has been found to be advantageous to keep the temperature of the flame as low as possible and to operate at flame temperatures below 1000° C., preferably at those below 800° C. The maintenance of a low flame temperature can be achieved, according to the invention, for example by the method of introducing into the flame inert gases, such as nitrogen, having a diluting effect. The application of this measure also leads to a decrease in the loading of the gas mixture with the compound to be decomposed and thus to a decrease in particle size of the ferromagnetic oxides formed, desirable in such cases.

For the maintenance of the favorable properties of the oxide particles formed with reference to the fineness and the surface development up to the separation or final recovery of the solid reaction products, it has been found to be extraordinarily advantageous to permit as complete a transition as possible of the ferric oxide produced in the process as aerosol, into the gel form, in the presence of the already coagulated portions, to take place. The particles at first separated from the aerosol state thus act, so to say, as an inoculating agent or condensation nucleus for the further separation of the portions not yet coagulated, inasmuch as they are kept in suspension in as long a path as possible. The coagulation is further favored by the fact that the particles are moved especially in relation to one another. According to the invention the gas stream containing the aerosol is whirled up in chambers of large volume or moved through long, purposely bent tubes up to 60 m. and more in length, in such a way that a preferably turbulent flow is developed and the suspended particles remain for some time, for example longer than 3 seconds, preferably 5 seconds or more, in the coagulation space. The final separation of the solid from the gaseous reaction products then takes place in auxiliary equipment, itself known, especially in cyclones. However, it is possible also to use filters or electrical separators. The advantage of the method of operation according to the invention lies primarily in the fact that it is possible to use even cyclones alone as the separation instrument, because, due to the previously described coagulation, the actual separation equipment is no longer burdened with the coagulation.

The invention is further clarified by the following examples:

(1) A gas mixture containing hydrogen, air, and nitrogen in the volume relationship 2.2 to 2.2 to 4 is mixed with sufficient vaporized ferric chloride so that the charge comes to 120 g. $FeCl_3/m.^3$ gas mixture. This homogeneous mixture is led to a tubular burner 24 mm. in diameter

of such a type that every hour 2.2 m.^{3} hydrogen, 2.2 m.^{3} air, and 4 m.^{3} nitrogen (all measured at standard condition of temperature and pressure) are passed through. By maintenance of a sufficiently high rate of outflow, e.g. 520 cm./sec. a flash back of the flame is prevented. The ferric chloride hydrolyzes practically quantitatively into Fe_2O_3, which is separated from the reaction gases after coagulation. The finely divided product is colored light yellowish brown and is strongly ferromagnetic. The rate of outflow is given according to a temperature of 20° C.

(2) A gas mixture containing hydrogen and air in the volume relationship 1.1 to 12.0 is mixed with vaporized ferric chloride to come to a charge of 120 g. $FeCl_3/m.^3$ gas mixture and burnt in the same burner as in the foregoing example. The rate of outflow was ca. 810 cm./sec. The finely divided product is colored light yellowish brown and is practically non-ferromagnetic.

Having thus disclosed my invention and described in detail illustrative procedure, I claim as new and desire to secure by Letters Patent:

1. Process for the preparation of finely divided ferromagnetic ferric oxide by decomposition of iron compounds in the gaseous phase, characterized by the steps of first homogeneously mixing a volatile ferric halide with water-forming gases, the gaseous mixture containing oxygen and hydrogen in at least sufficient amount for the formation of water for the complete hydrolysis of said ferric halide and hydrogen in excess of that amount, burning said mixture in a self-sufficient flame thereby completely hydrolyzing the halide to ferromagnetic oxide and thereafter separating the oxide from the products of combustion.

2. Process, according to claim 1, characterized by the fact that the gas mixture led to the flame contains hydrogen and air in the relationship 1:1.

3. Process, according to claim 1, characterized by the fact that the rate of discharge of the initial mixture leaving the burner opening comes to a multiple of its rate of flame propagation and that the burner flange is protected from the deposition of a tuft of finely divided oxide, by decrease of the ignition rate of the exit gases in its direct vicinity by flushing gases that flow in a thin layer past the burner flange.

4. Process, according to claim 1, characterized by the fact that the flame temperature is kept below 1000° C., preferably below 800° C.

5. The method of forming finely divided magnetic ferric oxide comprising mixing vapors of ferric chloride with hydrogen, oxygen and nitrogen in relative amounts such that upon burning water vapor is formed, the amount of oxygen being at least the stoichiometric equivalent of the ferric iron, the amount of hydrogen being in excess of the stoichiometric equivalent of the oxygen and the amount of nitrogen being sufficient to maintain a flame temperature of less than 1000° C., to form a homogeneous gaseous mixture, causing said mixture to flow from a burner by laminar flow at a rate at the burner in excess of the rate of flame propagation through said mixture, burning said mixture as it flows from the burner in a self-sufficient flame, thereby forming a flame containing water vapor as a combustion product and causing said ferric chloride to be hydrolyzed to ferric oxide by reaction with said water vapor, flowing the combustion products formed by said burning with the ferric oxide suspended therein in turbulent flow for at least three seconds, and thereafter separating the ferric oxide from said combustion products.

6. The method of forming finely divided ferro-magnetic oxide comprising forming a gaseous mixture containing relatively by volume 2.2 parts of hydrogen, 2.2 parts of air and 4 parts of nitrogen, mixing ferric chloride vapors with said gaseous mixture in relative amount of 120 grams per cubic meter and forming a homogeneous mixture, flowing said homogeneous mixture from a burner tube having an outlet diameter of 24 mm. at a volume rate per hour of 1008 grams of $FeCl_3$, 2.2 m.^{3} of H_2, 2.2 m.^{3} of air and 4 m.^{3} of N_2, and at a linear rate at the mouth of the burner of 520 cm./sec., burning said homogeneous gaseous mixture, and separating ferric oxide from the combustion products formed from said burning.

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