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[54] PROCESS AND MILL FOR GRINDING PULVERULENT MATERIALS, AND THE MATERIALS THUS GROUND

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[51] **Int. Cl.** **B02c 7/00**

[58] **Field of Search** 241/21, 43, 46.02, 46.06, 114, 241/132, 146, 252, 254, 220, 258, 255, 248, 290, 244, 184

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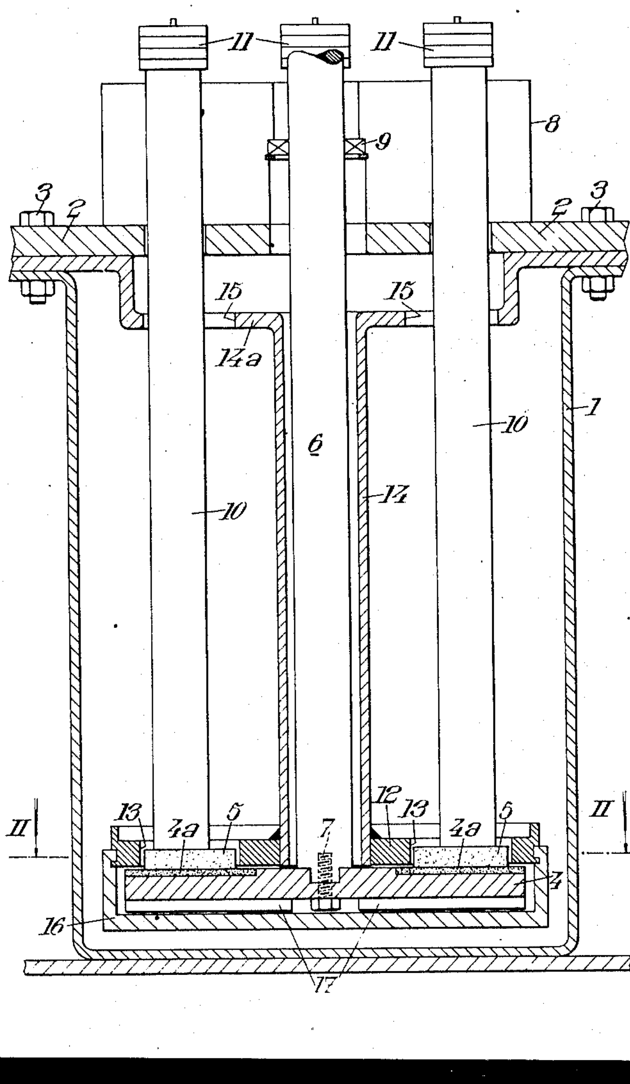
[57] **ABSTRACT**

The material or materials to be ground are put in suspension in a liquid, and this liquid is made to pass in a continuous and repeated manner between two rubbing surfaces. The pressure of application of one surface against the other is comprised between a few tens of g/cm^2 and a few kg/cm^2. One of the rubbing surfaces forms part of a horizontal disc driven by a vertical shaft, and the other rubbing surface comprises a plurality of stationary shoes resting on the disc. At least one of the rubbing surfaces can be made of the same material as the material to be ground.

7 Claims, 3 Drawing Figures



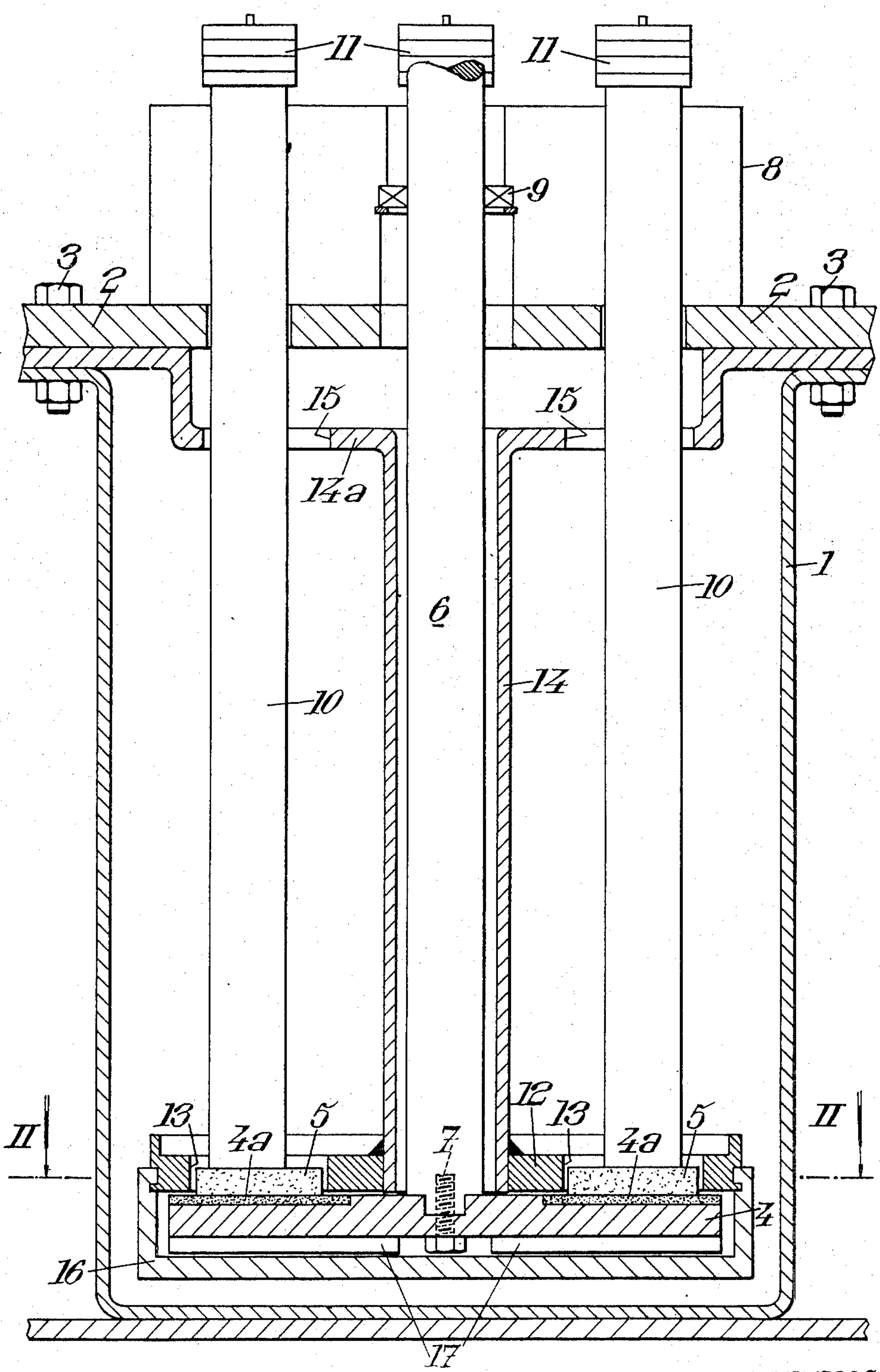


Fig. 1.

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Fig. 2.

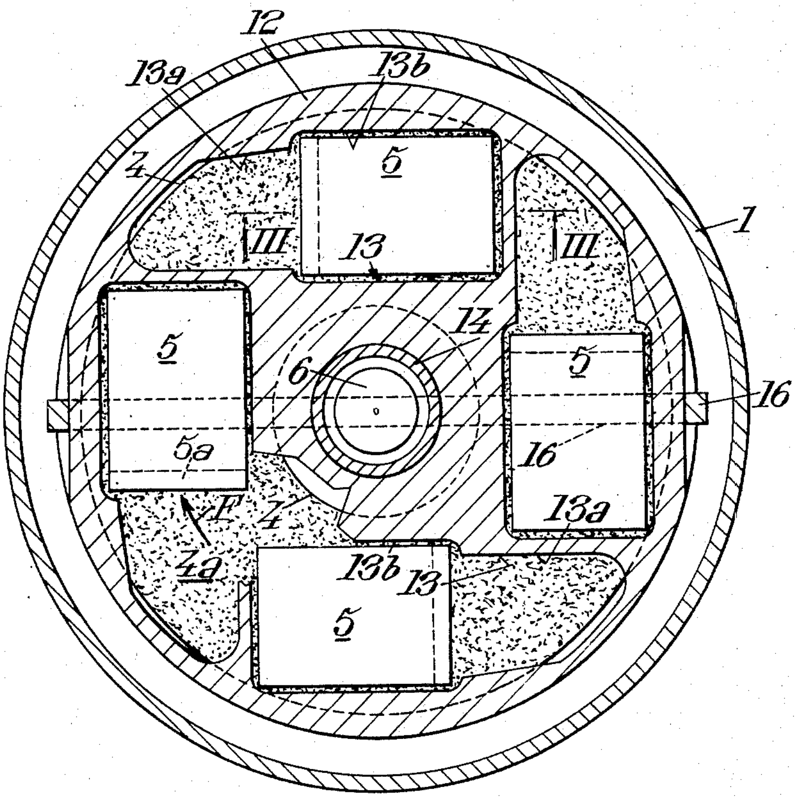
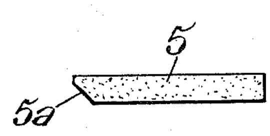


Fig. 3.



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PROCESS AND MILL FOR GRINDING PULVERULENT MATERIALS, AND THE MATERIALS THUS GROUND

This invention relates to processes and mills for finely grinding materials which are already in the form of grains of small dimensions, as well as to the fine powders obtained according to these processes and with the aid of these mills, and also to the products made with these powders, in particular by die-pressing and sintering.

In the prior art relating to the grinding of such grains, it is common to use mills which make use of shocks, such as, for example, ball mills. In the course of the grinding, the balls and the mill, no matter how hard they are, undergo a certain amount of wear. This has the disadvantage of adding to the grains undergoing treatment, the elements entering into the composition of the mill and of the balls, this addition taking place in a proportion which is greater as the time of grinding is longer and as the materials being treated are more abrasive.

Thus, the ball mills used in industry are generally made of steel, as are the balls that they contain. The steel is hardened by incorporating into it elements such as carbon, tungsten, chromium, molybdenum, vanadium, etc. It is true that due to these products of addition, the hardness of the steel is increased, and the wear of the mill and of the balls is decreased, but this wear, inevitable in spite of everything, causes the addition, to the materials undergoing treatment, not only of the principal constituent of the steel, that is to say iron, but also of the elements such as carbon, tungsten, chromium, etc., some of which can be very troublesome according to the properties that one has in view.

Another disadvantage of the prior art resides in the relatively large grain size of the powders obtained and of the constituent grains of the sintered products obtained from these powders.

Furthermore, in the preferred application concerned with the making of ferrites, it is difficult, starting from the metallic oxide powders coming from prior art grinding treatments, to obtain, after die-pressing and heating, bodies of very high density, of precise contours and free of defects.

The chief object of this invention is to mitigate these various disadvantages.

In accordance with the principal feature of this invention, the pulverulent material to be ground is put in suspension in a liquid which is not a solvent for this material, and this liquid, loaded with this material, is made to pass continuously and in a repeated manner between two hard parallel rubbing surfaces urged one against the other by elastic means or by gravity and driven with a relative movement parallel to these surfaces.

In a preferred embodiment which results in products of a very high purity, at least one of the rubbing surfaces is constituted of the same material as the material to be ground.

The invention will be able, in any case, to be well understood with the aid of the following complementary description and of the accompanying drawings, which complementary description and drawings relate to a preferred embodiment of a mill for carrying out the process of the invention.

In these drawings:

FIG. 1 is a longitudinal section of a mill for carrying out the process of the invention;

FIG. 2 is a section along II—II of FIG. 1, with parts cut away; and

FIG. 3 is a section along III—III of a part of FIG. 2.

According to this invention, in order to grind and possibly to mix materials which are in the state of grains in suspension in a liquid medium, the following or some similar procedure is adopted.

The liquid phase loaded with the grains is made to circulate in a continuous and repeated manner between at least two hard parallel surfaces facing each other, which are urged elastically one against the other and which are movable one with respect to the other.

In such a process, if the surfaces which face each other are relatively smooth, the grains are subjected to an action which is more akin to laminating than to abrading, and these grains are thus progressively reduced to smaller and smaller sizes, while the wear of the surfaces facing each other remains always a minimum. Moreover, if, as in certain preferred cases, the surfaces are of the same nature as the grains, the disintegration of these surfaces—whose wear remains relatively slight—will not introduce impurities into the treated product.

In order to carry out such a process, mills of various types can be used, in particular the embodiment which is going to be described hereafter.

According to this embodiment, the liquid carrying the grains is led to pass between a rotary disc and flat shoes resting on this disc.

The mill comprises a tank **1**, closed at the top by a cover **2** bolted by bolts **3**, the disc **4** mentioned above being provided horizontally in the lower portion.

This disc **4** is supported and driven in rotation by a vertical drive shaft **6**, on which it is fixed, for example by a screw **7**; this shaft passes through the cover **2**, is guided in a support **8** by at least one bearing **9** and is driven by a motor (not shown).

The shoes **5** are for example four in number and support freely rods **10** which, they too, pass freely through the cover **2** and the support **8** and can receive, at their emerging upper ends, weights **11** for regulating the pressure of contact of the shoes **5** on the disc **4**.

In order that the shoes **5** remain in place, a guide or perforated plate **12** is provided having four openings **13** passing therethrough from one side to the other so as to provide a passage for these shoes. The profile of the openings **13** is visible in FIG. **2**: it is constituted by a rear part **13*b*** following with play the rectangular shape of the shoes **5** and by a trapezoidal forward part **13*a***, in which the liquid is engulfed, as will be seen later on.

The guide **12** is fixed to the base of a fixed sleeve **14** surrounding the shaft **6**. This sleeve flares out at its upper portion **14*a***, where the rods **10** pass through thanks to openings **15** and where the cover **2** is fixed by the bolts **3**.

On the guide **12** is fixed a cross piece **16** fastened at two opposite points on the guide and whose role is to avoid rotation of the liquid as a whole.

As can be seen in FIG. 3, the forward face **5*a*** of the shoes **5** is bevelled towards the bottom in order to facilitate the penetration of the liquid between these shoes **5** and the disc **4**.

The surfaces of contact of the shoes **5** and of the disc **4**, or of a lining **4*a*** carried by this disc and facing the shoes **5**, are preferably constituted of a material such that in case of wear the products worn away from these surfaces do not constitute impurities for the mixture.

Thus at least one of the pieces **4** and **5** can be constituted or coated with a material of the same nature as that of the materials to be ground.

One of the rubbing surfaces can alternatively be coated with a layer of harder material. Nevertheless, neither of the two rubbing surfaces should be abrasive under the pressure used in the process.

By way of example, the disc **4** can be a conventional diamond-set grinding wheel whose surface has been rendered smooth by preliminary wear.

In the embodiment represented, the tank **1** is cylindrical and the shoes **5** are disposed in a circle about the shaft **6**. However the tank can have any desired shape permitting easy cleaning.

The operation of the mill described hereabove is the following.

The liquid in which the materials are in suspension is introduced into the tank. The disc **4** is set in rotation by means of the shaft **6** in the direction for which it leads the thus-stirred liquid to penetrate, through the openings **13*a***, between the shoes **5** and the disc **4** (arrow F).

In this space, the materials that the liquid contains are rubbed, crushed and finely pulverized. At the same time, the liquid serves as a lubricant for the rubbing of the rubbing surfaces.

The agitation of the liquid can be increased, for better stirring, by disposing an agitator or any other accessory, for example a helix, in the tank, which has the further advantage of ensuring a more intimate mixture of the constituents in the case in which there are more than one, and even of ensuring continuous circulation. This is the role of the flanges **17** of the disc **4**.

Although only a single embodiment has been represented, the rubbing surfaces can be arranged in a different manner so long as they remain freely applied one against the other (by gravity or by other elastic means) along insignificant areas.

Thus the disc **4** could be replaced by a cone or a cylinder rotating about its axis and the shoes **5** by shoes having complementary conical or cylindrical rubbing surfaces.

Furthermore, the shoes **5** could also be made to move, either in rotation about themselves, or in rotation about the shaft **6**.

The regulable application pressure of the surfaces one against the other can be relatively low and is preferably comprised between a few tens of grams per cm^2 and a few kilograms per cm^2.

The degree of dilution of the starting powder should be such that the loaded liquid remains fluid and not pasty, the weight of powder per unit volume being preferably comprised between 20 and 200 grams per liter.

By way of example, two examples for carrying out the invention will now be given.

EXAMPLE 1

In order to obtain yttrium-iron garnet of formula 3 y_2O_3, 5 Fe_2O_3, the powders of iron oxide Fe_2O_3 and of yttrium oxide Y_2O_3 are put in suspension in water in the molecular proportion corresponding to the above garnet formula and in the amount of 100 g of the mixture per liter. The disc is constituted by a worn diamond-set grinding wheel. The shoes **5** are constituted by blocks of yttrium-iron garnet. The mean linear speed of the disc is 9 meters/second (m/s) and the application pressure of the shoes **5** on the disc is 100 g/cm^2. After 72 hours of operation, the suspension is collected in a heated receptible in order to make the water evaporate.

The dry powder obtained is exceptionally fine (grain size very much smaller than 0.1 micron), pure and homogenous.

In order to constitute a sintered product from this powder, it is first compressed in an appropriate die.

It has been found that this operation can be executed without any binder and with very high pressures (20 to 25 metric tons/cm^2 (t/cm^2) or more) without observing the cracks or other defects which manifest themselves in the raw die-pressed products made from known powders at relatively low pressures (1 **t/cm²**).

It has also been found that, for the above composition, raw die-pressed products can be obtained (before heating) with a density equal to or even greater than **4**, whereas with known powders of the same composition, the maximum density for the raw products was 3.40.

Another advantage is that the die-pressing pressure can be chosen in order to regulate the density of the raw die-pressed product.

The raw die-pressed product is then heated to 1,250° C for 4 hours in oxygen, and a garnet is obtained whose grains measure about 2 microns and whose specific mass is 5.15 g/cm^3: as the theoretical specific mass of this garnet is 5.17 g/cm^3 the porosity is only 0.4 percent.

Comparatively, with conventional methods of co-precipitation or of grinding in a ball mill, the operation is much longer and it is necessary to use high temperatures for the sintering in order to obtain low porosity: for example, for the porosity to be lower than 2 percent, the sintering temperature must exceed 1,400° C.

EXAMPLE 2

A mixed ferrite of nickel-zinc of formula $Ni_{0.5}Zn_{0.5}Fe_2O_4$ is obtained by grinding in an aqueous medium the constituent oxides for 24 hours in the mill of Example 1 (with the shoes **5** constituted of this mixed ferrite of nickel-zinc and under a contact pressure about the same as previously), then by die-pressing and thermal treatment for 24 hours at 1,150° C. The specific mass of the product obtained is 5.30 g/cm^3, which corresponds to a porosity of 0.4 percent, whereas with a conventional grinding mill, a porosity of 3 percent is obtained after 14 days of grinding and 10 days of thermal treatment at 1,200° C in oxygen.

The present invention permits the grinding and the mixing of the pulverulent materials to be carried out with numerous advantages with respect to the prior art processes, and in particular the following advantages:

— if the mechanical part is constructed with a little care (but following the rules of mechanics which are completely conventional, nothing more), the process described is very quiet, incomparably quieter than ball mills (or mills using shocks in general);

— with a mill of suitable size, this process can be carried out either on small quantities or on large quantities, with identical results;

— this process can replace not only the other grinding processes, but also chemical co-precipitation, and this is very advantageous for the present process is applicable to any composition;

— this process permits the purety of the primary materials to be safeguarded absolutely;

— the powder obtained can have a very high fineness (thus it is possible to obtain powders of common metal oxides: iron, manganese, nickel . . . with a fineness such that their time of sedimentation in water exceeds several weeks);

— the powder obtained is formed of grains having a much more homogenous grain size that can be obtained with conventional grinding processes;

— one of the most important advantages of this process is the aptitude that the powder obtained has for undergoing the subsequent operations of die-pressing and sintering: first the die-pressing is much easier and does not require any binder; furthermore, even sintering at low temperature provides a sintered material of high density, this density exceeding any that can be obtained with a ball mill and sintering in the same conditions; it is thus possible to obtain a material of high density which has a sufficiently fine grain size, whereas these two qualities are normally contradictory; it is also possible to use the die-pressing pressure as a parameter for regulating the final density (or the porosity);

— the relative density (with respect to the theoretical density calculated from the atomic masses and from the spacing of the crystaline network) of the raw product, after die-pressing, can already be very high; consequently, the shrinkage in the course of sintering is much smaller, which constitutes an important advantage for the mechanical precision and for the mechanical resistance of the finished pieces;

— possibly, and independently of any consideration of the size of the grains, this process can be used for increasing the reactivity of a product.

In the case in which the powders according to this invention serve for the making of ferrites, these ferrites have considerably improved qualities due to their density as well as due to the fineness and the regularity of their grains, in particular with respect to the widening of their band of linear operation for certain hyperfrequency applications, the precision of their sides (an appreciable advantage for example for heads for reading magnetic tapes), and the quality of the permanent magnets which can be made from them.

Needless to say, the invention is not limited to the particular application and embodiments which have been described more particularly; on the contrary, this invention embraces many modifications.

What we claim is:

1. Apparatus for preparing a pure fine powder from a pure, hard, homogeneous, pulverulent material in suspension in a liquid, comprising: a receptacle for containing said suspension, at least one pair of first and second hard and smooth twodimensionally parallel rubbing surfaces disposed facing one another within said receptacle and means urging said rubbing surfaces resiliently against one another; means for providing movement of first and second surfaces with respect to one another parallel to each other, a shoe providing said first rubbing surface, said shoe being held substantially stationary with respect to said movement and having an upstream edge (with respect to the relative direction of flow of the liquid in which the shoe is immersed) so shaped as to facilitate the introduction of the suspension between the two rubbing surfaces, wherein said second surface is the upper face of a horizontal disc rotatable about a vertical axis.

2. Apparatus according to claim **1**, including a fixed perforated horizontal plate having openings in which the shoes are located and guided.

3. Apparatus according to claim **2**, comprising vertical rods resting on the shoes and loaded by weights, whereby said first and second rubbing surfaces are urged against one another.

4. A grinding mill comprising in combination,

a horizontal disc having an upwardly facing grinding surface for rotating about a vertical axis,

a vertical shaft driving the disc in rotation,

a plurality of stationary shoes having downwardly facing grinding surfaces in grinding relationship with the grinding surface of said disc,

a tank means surrounding said disc and shoes for containing a liquid suspension of material to be ground,

a vertically extending rod secured to each of the shoes for applying a downward force thereto, and

a horizontal stationary plate within the tank having openings therein,

said openings shaped to receive the shoes and hold them in stationary position on the disc as the disc rotates therebeneath,

said openings passing said liquid suspension downwardly to the area between said grinding surfaces of the shoes and plate.

5. A grinding mill constructed in accordance with claim **4**, wherein said disc has projecting flanges for circulating the liquid in the tank to cause it to pass upwardly into said openings in the plate.

6. A grinding mill constructed in accordance with claim **4**, wherein said plate has surfaces at the trailing edges of the openings relative to the rotation of the disc which engage the trailing edges of the shoes to hold them in stationary position and said openings have large open areas in advance of the shoes for passing said liquid suspension.

7. A grinding mill constructed in accordance with claim **4**, wherein said shoes have a bevelled edge facing toward the direction of rotation of the disc so as to facilitate the introduction of the liquid between the shoes and the disc.

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