United States Patent

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[54] METHOD AND APPARATUS FOR COMMINUTING AND REACTING SOLIDS

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[52] **U.S. Cl.** **241/27**, 241/182

[51] **Int. Cl.** **B02c 17/16**

[58] **Field of Search** 241/18, 27, 172, 182, 183

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[57] **ABSTRACT**

The grinding or comminution of solids, such as metal powders, and certain inorganic substances in the absence of a liquid continuum is accomplished at a relatively rapid rate in activated media of high momentum and low ball pressure, by rotating one or more rigid agitators through a relatively flat but properly proportioned (depth to diameter), bed of grinding media, such as relatively small balls, pebbles, etc. at a sufficiently high speed to cause the apparent volume of the grinding media to increase substantially in the agitated condition over that in the unagitated condition. The mean free paths between contacts of separate elements of the grinding media are therefore greatly increased, and the peening or burring energy applied to the material in process by contact between separate grinding elements is enlarged because of the increased momentum of contact. Unique chemical or structural properties are obtained in the comminuted product, especially when the dry grinding is continued beyond the point where appreciable decrease in average particle size occurs. Means is also provided in the apparatus to decrease or prevent caking of the partially ground material in portions of the apparatus.

21 Claims, 11 Drawing Figures

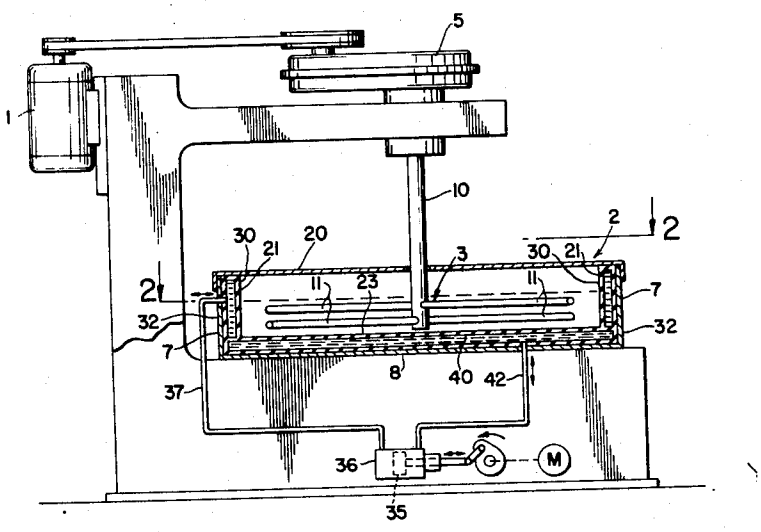


FIG. 1

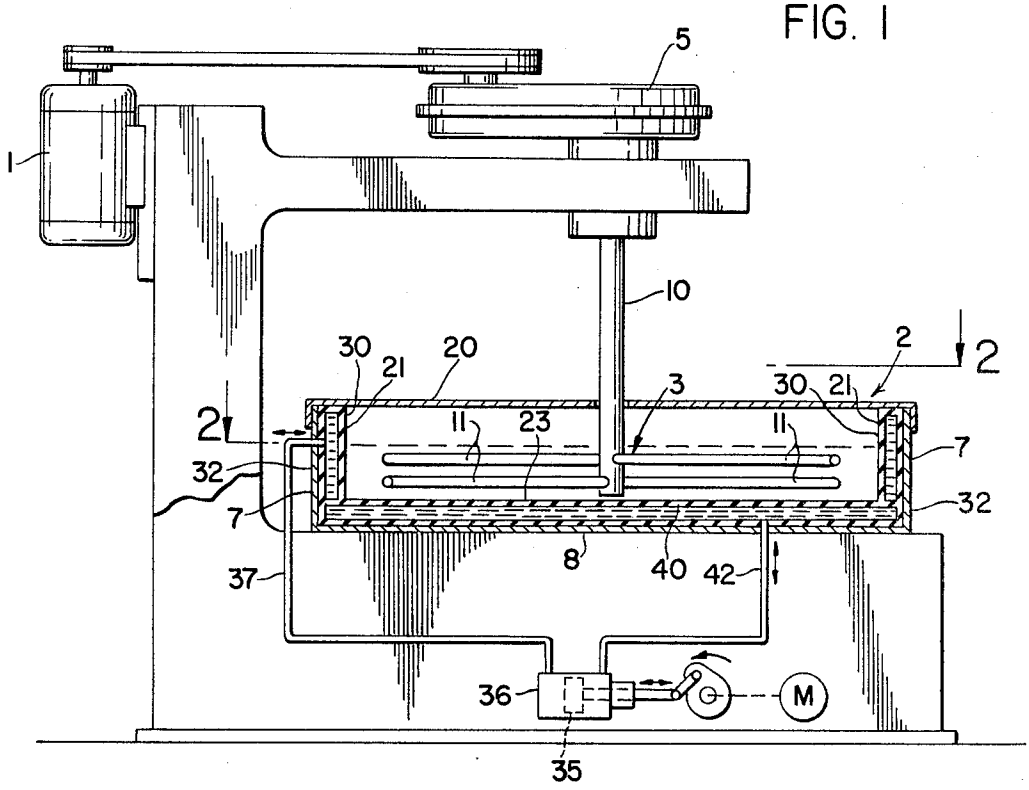
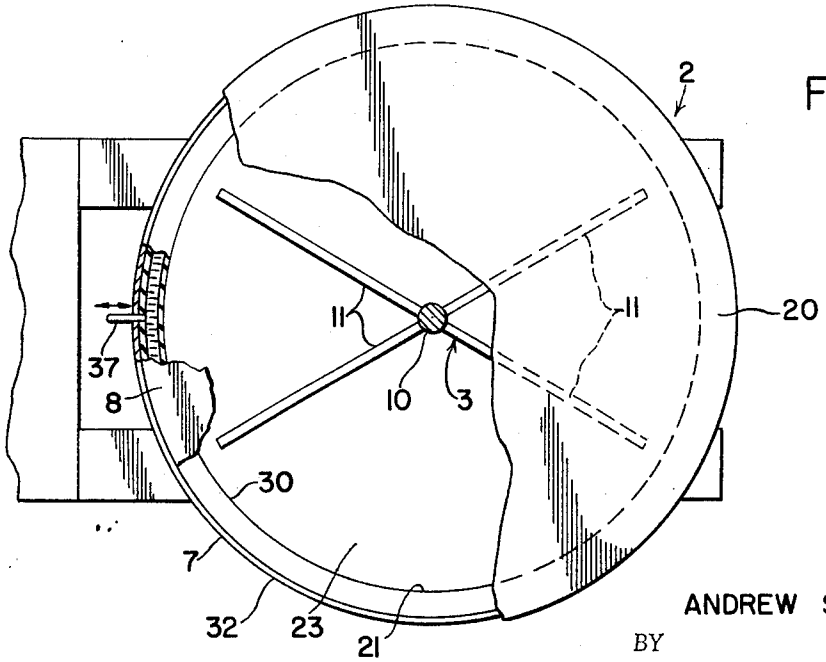


FIG. 2



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FIG. 3

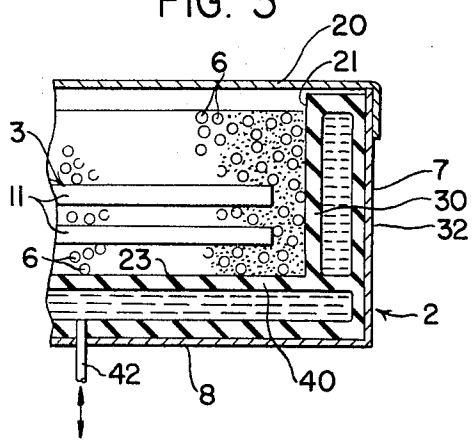


FIG. 4

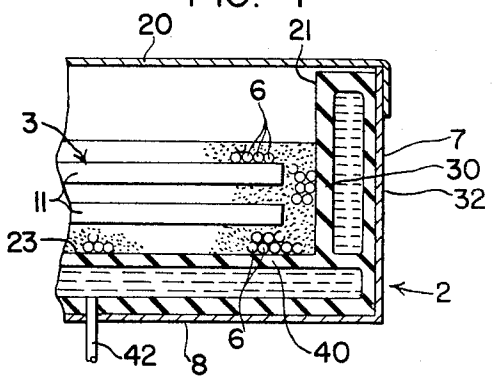
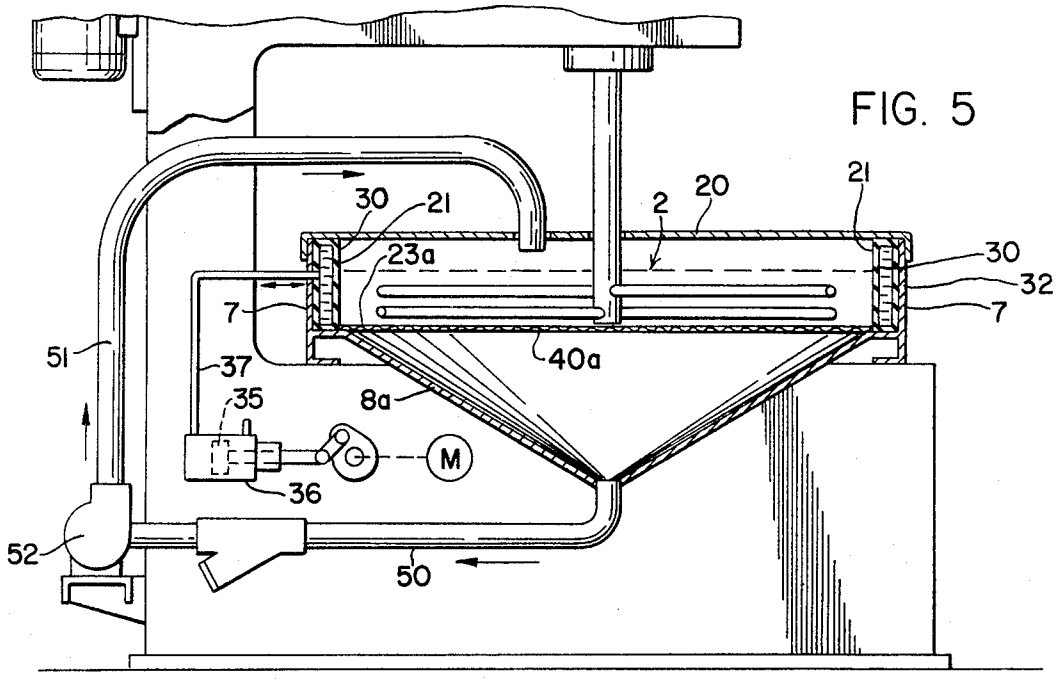
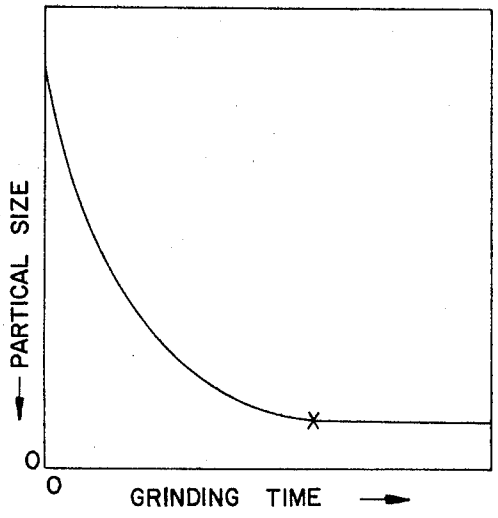


FIG. 5



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FIG. 6



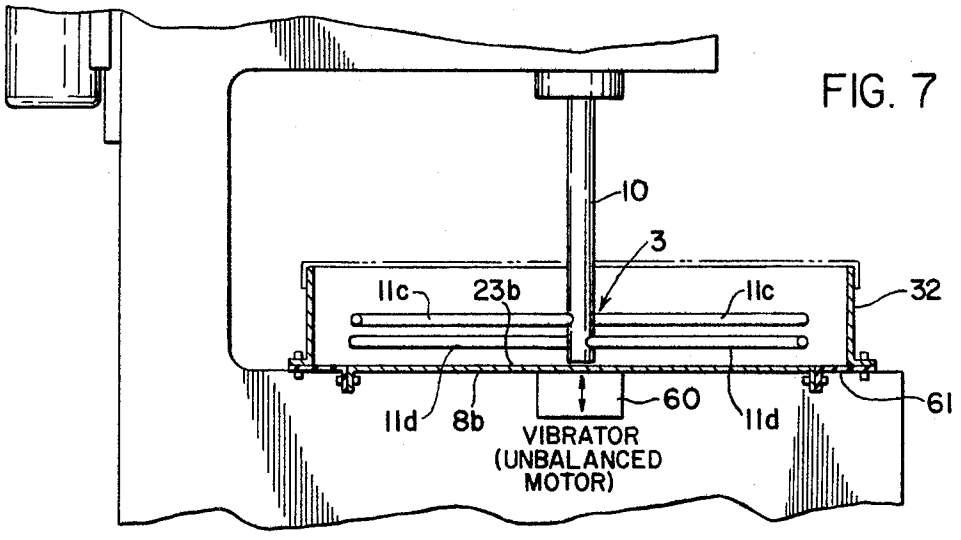


FIG. 7

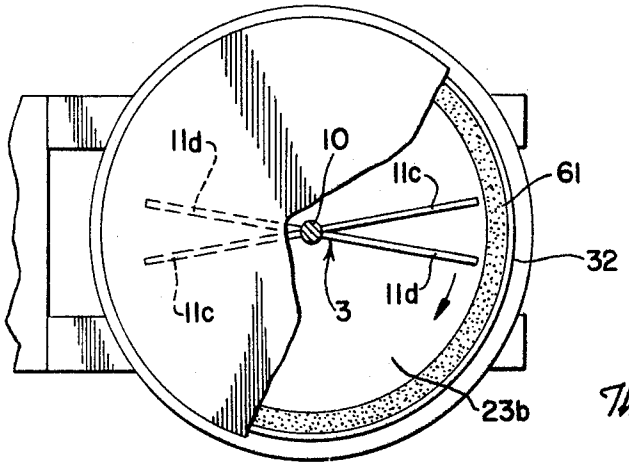


FIG. 8

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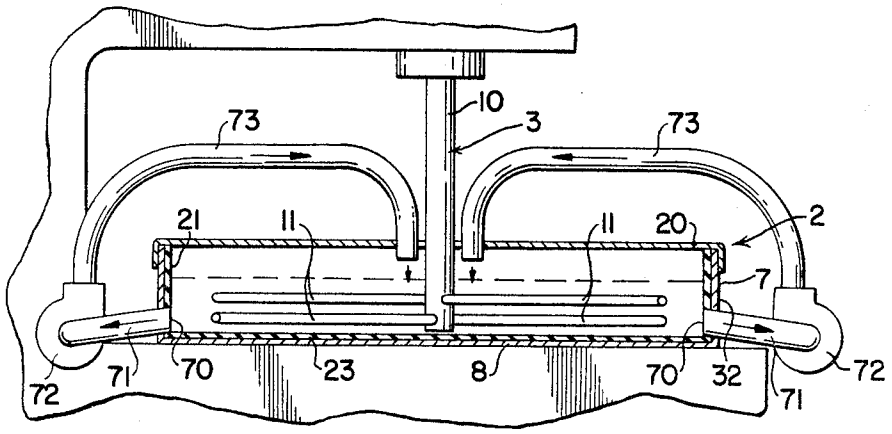


FIG. 9

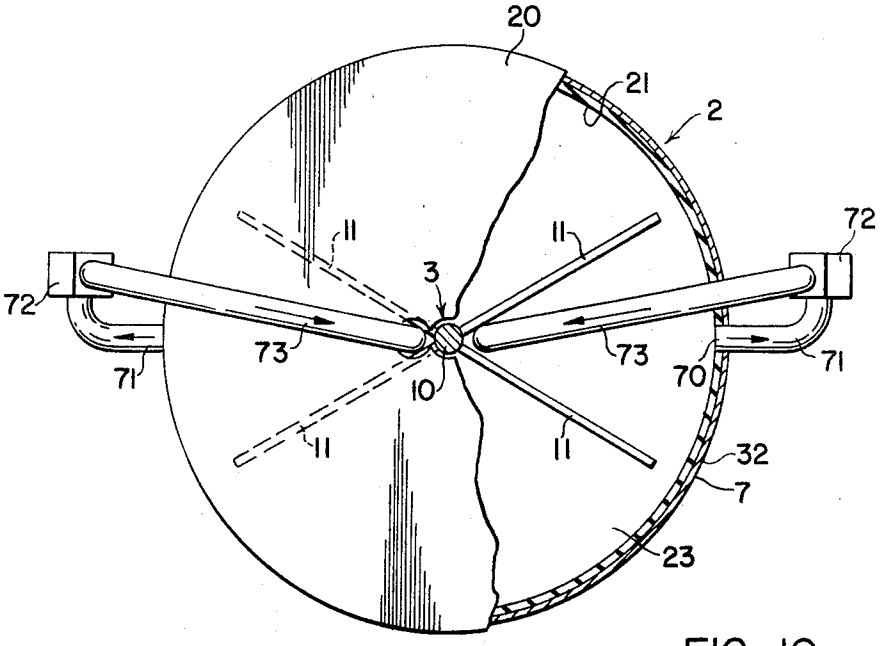


FIG. 10

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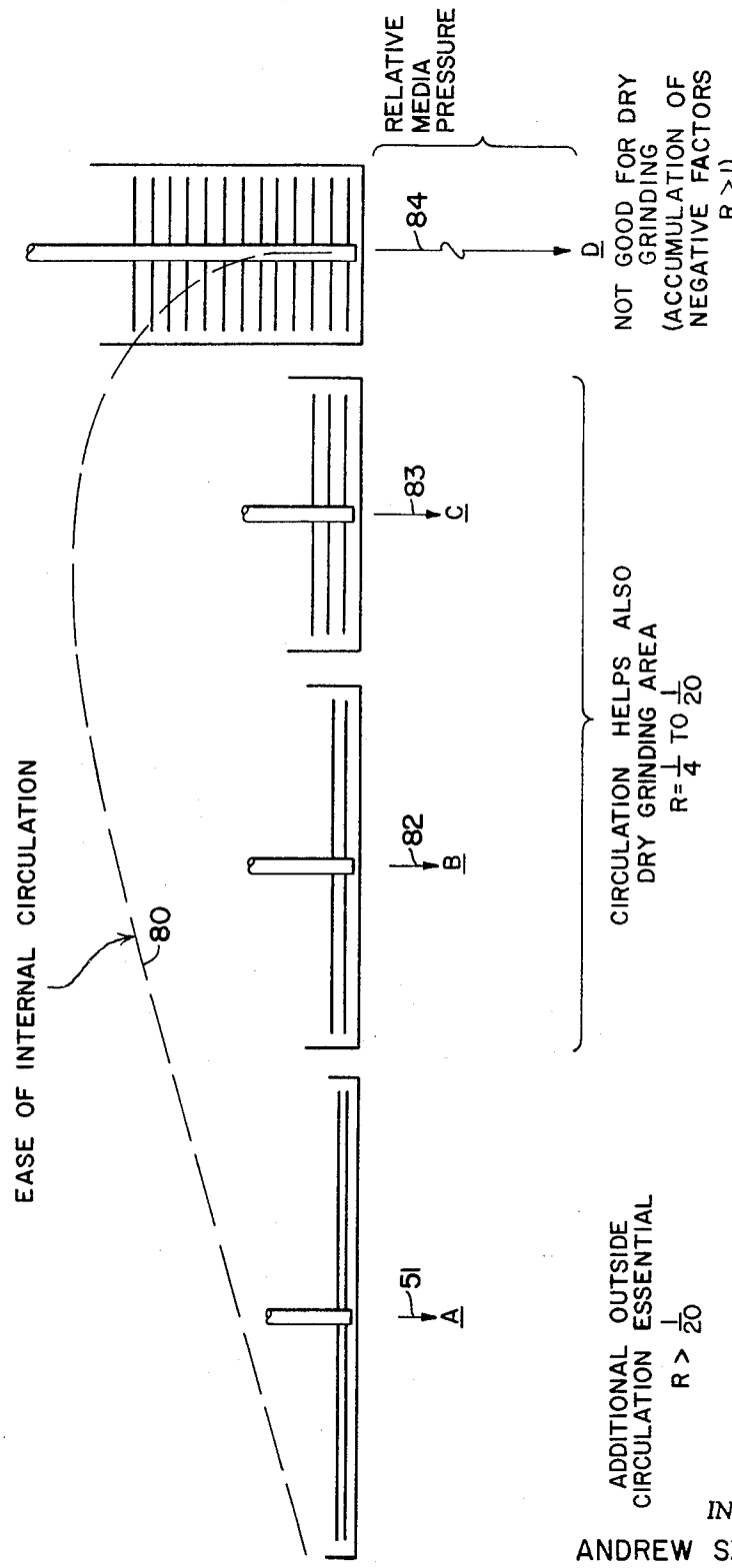


FIG. 11
INFLUENCE OF ASPECT RATIO R (i.e. RATIO OF DEPTH TO DIAMETER OF BED OF GRINDING MEDIA)

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METHOD AND APPARATUS FOR COMMINUTING AND REACTING SOLIDS

The present invention relates to a process and apparatus for grinding or comminution of solid substances. It particularly relates to a process and apparatus for grinding of solids in the substantial absence of a liquid continuum.

The grinding of solids is usually accomplished by rubbing and/or peening the material to be processed (the processed mass) between elements of agitated media, such as balls, pebbles and the like. The energy imparted to the processed mass is a function of both the relative velocities of the contacting elements of the media, i.e. the balls or pebbles, their individual masses, and the number of points of contact.

When grinding occurs in the ball mill, for example, the mean free space for relative movement between contacting elements of media before contact is made is very small. The relative velocities of the contacting elements of the grinding media, is, therefore, necessarily very low. To obtain reasonable energy at contacting points, the mass of the elements must be relatively large, resulting in a comparatively few grinding contacts per unit of volume. In order to increase the contacting points to a reasonable, practical value, size of the elements is limited; hence the energy imparted to the processed mass by the peening action is also limited. Grinding efficiency, grinding energy imparted, and speed of comminution are low.

If the grinding media were the size of single molecules the energy wasted as heat dissipated in the interior of the elements of grinding media would be about zero, as in the case of an ideal gas. However, since the elements of the grinding media necessarily comprise many molecules, a great portion of all energy employed is dissipated as heat internally of the elements of grinding media. The smaller the individual elements per grinding contact, the less is the proportion of the energy dissipated as heat internally of the grinding elements and the greater the grinding efficiency or proportion of energy applied to the processed mass.

In my prior patents, including U.S. Pat. Nos. 2,764,359 3,131,875 and 3,149,789, and British Pat. No. 716,361, I described apparatus for and a method of grinding wherein the grinding media, such as balls or pebbles, is maintained in such an agitated condition that there is a greatly increased mean free space or path for movement of individual elements thereof between contacts. This is accomplished by rapidly moving or rotating one or more arms or rigid agitators through a bed of grinding media. The speed of movement is such as to cause the bed of grinding media to apparently substantially increase in volume. The result of such procedure is to increase the relative potential velocity of the individual elements (balls, pebbles, etc.) with the result that much smaller grinding elements may be utilized, still maintaining or even increasing the kinetic energy applied at each contact. Both the grinding contacts and energy imparted per contact may be thus greatly increased and with the result that grinding speed is greatly increased over that of prior methods.

While I stated in one or more of the aforementioned patents that the apparatus described therein might be used for dry grinding of solids, it was primarily used for and adapted for grinding of solids in a liquid continuum. Although by the use of apparatus and method described in my aforementioned patents, the potential relative velocities of the individual elements is greatly increased over those of ball mill-type apparatus, when the grinding of solids occurs in a liquid, the liquid greatly reduces the relative velocity between elements of the grinding medium, prior to contact, resulting in loss of energy available to particles being ground.

When material is, however, ground in the absence of a liquid continuum, several difficulties have arisen. There is an absence of the hydrodynamic action caused by the flow of the liquid that insures distribution of materials being processed, and materials tend to settle and cake out in dead spaces and not participate in the processing. Also, the amount of material that can be processed in a given volume of processing tank or bed of grinding medium is very much smaller in the absence of a liquid continuum, being about one-half that processible in the presence of a liquid continuum. The horsepower requirement per pound of material in process is therefore much greater.

I have found, however, that unique chemical or physical products are produced by the dry grinding of many solids under certain conditions, such as relatively high velocities imparted to the elements of the media, large mean free paths between contacts of the grinding elements, and limited volume of material in process. This is especially the case when the grinding is more prolonged than is indicated by decrease in particle size.

It is an object of the present invention to provide apparatus especially suitable for the grinding of solids in the absence of a liquid continuum, which apparatus requires much less horsepower than formerly required and which has much greater efficiency.

It is another object of the present invention to provide apparatus especially suitable for dry grinding of solids, wherein the settling-out or caking-out of the partly ground solids is eliminated.

A further object of the present invention is to provide a method of grinding solids in the absence of a liquid continuum wherein higher velocities are applied to the elements of the grinding media and greater grinding efficiency and less power is required than heretofore.

A further object of the present invention is to provide a method of treating and comminuting solids or mixtures of solids to cause desirable structural changes or reactions in the comminuted product obtained.

Other objects will be apparent from the following description of the invention, suitable apparatus of which is illustrated by the accompanying drawings, in which:

FIG. 1 is a schematic elevational view, with parts broken away, of one form of apparatus suitable for the present invention;

FIG. 2 is a view on the line 2—2 of FIG. 1;

FIG. 3 is a vertical sectional view through a portion of the apparatus of FIG. 1, showing the grinding media and processed mass therein at the enlarged volume associated with the operation of the device;

FIG. 4 is a similar vertical sectional view through a portion of the apparatus showing the processed mass and grinding media when the device is not in operation;

FIG. 5 is an elevational view with parts broken away of a portion of a modified form of apparatus showing a modified form of container for the grinding media;

FIG. 6 is a typical curve showing particle size versus grinding time; and

FIG. 7 is an elevational view, partly in section, of a portion of another modified form of apparatus showing the empty grinding container with a movable bottom member and an attached electrically operated vibrating means; and

FIG. 8 is a top plan view, with parts broken away, of the apparatus of FIG. 7;

FIG. 9 is a schematic, elevated view with parts broken away and partly in section of a preferred modified form of the grinding portion of apparatus;

FIG. 10 is a plan view of the portion of the apparatus of FIG. 9;

FIG. 11 is a schematic representation of the influence of aspect ratio (i.e. depth to diameter ratio) of the unagitated bed of grinding media on ease of internal circulation, media pressure and relative adaptability for dry grinding.

Referring more particularly to the drawing, wherein like numerals of reference are used to designate like parts throughout the several views, apparatus embodying the present invention comprises a container 2, preferably of cylindrical shape and having a substantially vertical axis, an agitator 3 rotatable about a vertical axis and having suitable driving means 5, which may comprise a motor 1 suitably connected to drive the agitator, a bed of ball-like grinding media, such as a mass of unconnected, relatively movable dense balls or pebbles 6 contained in the container 2, and generally means for automati-

cally preventing the accumulation of agglomerated or caked, dry, partially ground process material in certain parts of the apparatus.

The container has a continuous cylindrical wall **7** which has an outer rigid cylindrical portion **32**, usually of metal, a bottom that has an upper surface **23** and a lower surface member **8**, and preferably a suitable cover **20**. The bottom and sides co-act to form a container to support grinding media and process material. The cover **20** may or may not be present, but, when present, co-acts with the sides and bottom to form a closed chamber.

The agitator **3** is rotatable relative to the container **2** and comprises a vertical, axial portion **10**, with one or more pairs of rigid arms **11**. The arms of each pair extend symmetrically outwardly from opposite points at the lower region of said shaft and extend from opposite points on said shaft, preferably radially therefrom and preferably the axes thereof lie in a single plane perpendicular to said shaft. The arms **11** are rotatable with the axial portion **10** and preferably extend in a radial direction toward the relatively vertical or cylindrical inner surface **21** of the sidewall **7**. To prevent possible jamming of elements of grinding media between an arm and the sidewall of the container, it is usually desirable that the ends of the arms **11** be spaced from the inner surface **21** of the sidewall of the container by a distance of at least two and preferably five to 10 diameters of the separate elements **6** (balls or pebbles) of the grinding media to be used. The lowermost of the bars or pairs of arms **11** is spaced from, but relatively near the upper surface **23** of the bottom; the successive pairs of oppositely extending arms are spaced vertically with respect to adjacent arms and may be positioned angularly, as desired, with respect to the next lower or preceding pair of arms. However, it is preferred if more than one pair of arms **11** are used that the next successive higher pair of arms be angularly spaced so as to accentuate the lifting effect of the next lower pair. As shown particularly with respect to the modification of FIGS. **7** and **8**, this is accomplished by positioning the next higher pair of arms **11c** at an angle such that it slightly follows the next proceeding lower arm **11d** in the direction of rotation of the agitator.

One to three pairs of oppositely and symmetrically disposed arms **11** may be used in the agitator **3**. The lowermost pair of arms **11** is disposed to lie within the bed of ball-like grinding media and is preferably spaced from the upper surface **23** of the bottom of said container **2** by more than one diameter of said ball-like elements.

Whereas in the apparatus disclosed in my aforementioned prior patents the ratio of depth of the container **2** (or height of sidewall **7** of the container) to diameter of the container is **1** or more, in the apparatus of the present invention, the ratio of depth of container to diameter is 1:2 to 1:10, and preferably about 1:5 or 1:6. In the unagitated condition, the depth of the flat bed of grinding media, which consists essentially of the balls or pebbles **6**, is usually about one-half of the height of the sidewall of the container above the bottom thereof. The ratio of depth of bed of grinding media to diameter is about one-fourth to one-twentieth, and preferably one-tenth to one-twelfth in the unagitated condition.

Since the resistance to movement of the arms through the mass of grinding media is determined in very substantial measure by the depth of the mass of grinding media above said arms, it is seen that by using a relatively flat bed of grinding media as described above that the power requirement is very much less than the power requirement for the apparatus described in my aforementioned patents. In the presence of a liquid continuum the weight of the mass of the grinding media is compensated in substantial measure by the buoyancy of the liquid on the balls or pebbles, but such is not the case during dry grinding.

The optimum net ball or pebble pressure at the bottom of the bed is found to be around 800 grams per square centimeter, although excellent grinding speeds are obtained at ball pressures between 500 and about 1,000 grams per square centimeter and as low as 200 and as much as 1,200 grams per square centimeter. The net ball pressure, B.P., is computed by the following formula.

$$\text{B.P.} = (\text{Depth of bed in centimeters}) \times (\text{Density of ball material less density of continuum}) \times (\text{Packing factor})$$

The packing factor is 0.67 for spherical balls. The density of steel balls is approximately 7.6. Thus, with a bed depth in unagitated condition of 20 C.M., using steel and no liquid continuum, ball pressure, B.P., would be $20 \times 7.6 \times 0.67 = 1{,}008.40$ grams per square centimeter.

In the dry grinding of solids, including metals, there is as above discussed a tendency for the partially ground portions to build-up cakes or layers on surface portions which are most removed from intensive agitation. In accordance with another preferred feature of the apparatus of my invention, means is provided to eliminate all or most of such build-up and return the partially ground solids to the processed or processing mass. This is accomplished by providing resilient surfaces where build up normally would occur, by flexing or vibrating surfaces where build up or caking normally would occur, by permitting flow of process material through the supporting surfaces and returning it or recirculating it to the grinding media or by circulating both process material and grinding media.

In accordance with the apparatus of FIGS. **1** and **2**, the cylindrical wall **7** of the container comprises a rigid outer, generally cylindrical wall portion **32**, and suitably carried over the inner surface of the outer wall portion **32**, a flexible vibratable member **30**, usually of tread rubber, having an inner cylindrical surface **21**. The flexible member **30** is suitably attached to or carried by the inner surface of the wall **32** to form a liquid-retaining cavity, as shown. Means, such as the oscillating piston **35** in the cylinder **36** is provided to cause fluid flow through the tube **37** into the cavity formed between the members **30** and the rigid wall **32**, and thus to cause periodic flexing of the member **30** to remove caked material that has formed thereon.

The bottom of the container similarly comprises the lower rigid member **8**, which is usually of metal, and a co-acting flexible member **40**, which is usually of tread rubber, with an upper, generally flat surface **23**. The flexible member **40** is attached around its periphery to the upper surface of the rigid member **8** to provide a fluid-retaining cavity. The tube **42** is connected both to that cavity and to the cylinder **36**, so that by oscillation of the piston in the cylinder **36**, fluid therein is forced periodically in and out of the cavity to cause flexure of the member **40**. This serves as means for removing caked material from the upper bottom surface **23**.

Referring more particularly to the modification shown in FIG. **5**, the container **2** is similar to that shown in FIG. **1** except that the bottom portion thereof comprises a disc-like porous member, such as the screen **40*a*** having an upper surface **23*a*** to support the grinding media thereon. A true bottom **8*a***, preferably of inverted conical shape and nonporous, is provided under the screen to accumulate partially ground materials that pass through the screen. This is continuously returned to the upper portion of the container **2** by any suitable means, such as a conveyor comprising the tubes **50** and **51** and the motor-operated transport device or blower **52**.

In the modification shown in FIGS. **7** and **8**, the bottom member **8*b***, having an upper surface **23*b*** to support the grinding media and the process material, is provided with suitable mechanical vibrating means **60** (shown schematically), such as an unbalanced motor which operates at high speeds, or another mechanical vibrator suitable for effectively vibrating the rigid bottom **8*b***, preferably in at least an axial direction.

To permit relatively free movement of the disc-like bottom member **8*b*** in an axial direction, the bottom member **8*b*** is attached to the side member **32** at the base thereof, along its entire periphery, through a flexible annulus **61** of rubber or similar material. The outer periphery of the annulus is con-

nected to the lower portion of the cylindrical sides **32** of annulus container **2**, and the inner annular surface of said annular **61** is suitably connected to the rigid disc-like bottom portion **8***b*, which is preferably of metal. The vibration of the bottom portion **8***b* cause caked material to be disengaged from the upper surface **23***b* thereof and returned to positions where grinding or reactions due to the energy of impact of the grinding media occurs.

In the comminution of solids in accordance with my invention, the container **2** is preferably filled about one-third to one-half full of ball-like grinding media, such as small hardened steel balls, pebbles and the like. The elements of grinding media are preferably of about uniform diameter. Inasmuch as the energy at impact, the peening energy expended on the process material, varies as the square of the velocity, the mass required in the separate elements **6** of grinding media for effective grinding and for procuring dry reactions at particle surfaces is largely determined by velocity obtained which is dependent on mean free space or increase in apparent volume of the flat bed upon agitation, which in turn is at least partly dependent on the speed of the movement of the bar or bars (the pair or pairs of arms **11**) through the flat bed. Also, the more dense the elements **6**, the smaller is the size required for given effects. The elements **6** are, therefore, of highest density practicable and generally selected to be less than one-half inch in diameter and are most generally around one-fourth or three-sixteenth inch in diameter, or even smaller. The particle size of the grinding material and the distribution curve depends both on the size of material to be ground and the size of grinding media used. Smaller media require higher speeds to provide the same impact energy but provide smaller particle size and a sharper distribution curve. It is often desirable to grind in stages i.e. to utilize larger balls in the first stage to reduce the material substantially and then to finish grinding with smaller media.

A relatively small amount compared to the weight of the balls of the granular or coarse powdery material that is to be ground or reacted in the dry state is added to the container **2**. The amount of material to be ground (process material) is generally about one-fifth to one twenty-fifth of the weight of the grinding media, i.e. the balls or pebbles. Often the weight of the material to be ground is preferably from one-tenth to one-twentieth of the weight of the balls and in the absence of a liquid continuum the amount of process material is always less than one-half that which would be present if grinding occurred in the liquid slurry used in accordance with prior practices. The agitators are rotated at a speed sufficient to cause an appreciable enlargement in the apparent volume of the flat bed of grinding media and process material. Usually there is at least a 20 percent increase in apparent volume when the apparatus is in efficient operation. Generally, speeds are about 100 to 500 or 600 rpm and as high as 1,400 rpm. may be used. Speeds in the range of 100 to 700 rpm or preferably between 200 and 600 rpm are generally found to be more desirable. The maximum speed of course depends upon the diameter of the container and size of grinding media used.

In the dry grinding of reactive solids such as metal powders, it is important to provide a blanket or atmosphere of a suitable inert gas. Nitrogen is usually the gas of choice but in the case where nitrides are readily formed a blanket of helium argon may be used. In some cases a blanket of hydrogen is most desirable.

It is found that the average time for a given reduction in particle size is about one-fifteenth to one-twentieth that required by a ball mill. Also, I have found that unique results occur in many cases, apparently because of the higher impact energy, particularly when grinding takes place for a substantial time after no appreciable reduction in particle size occurs. Thus, referring to the drawing of FIG. **6**, grinding would ordinarily be terminated at the time "X" where the curve of particle size vs. time becomes substantially parallel. On continued operation past the point X no appreciable reduction in fineness occurs. I have found, however, that by continuing the grinding operation for a substantial period, usually of the order of one-half hour or longer, past the point marked X in FIG. **7**, where a substantially maximum fineness occurs, that unique results are obtained in many solids, including metal powders such as powdered nickel, chromium, cobalt and iron, particularly in mixtures of two or more of these metal powders, and in metal oxides such as in magnetic iron oxides and bariumated iron oxides, such as are used in making magnetic components of refrigerator gaskets and the like. There is apparently a selective agglomeration at certain crystal faces because of the energy imparted during attempts to continue comminution in the apparatus described above. The selective agglomeration at certain selected crystal faces apparently results in structure-oriented solids which have unique properties. Thus, in the case of iron oxides which are used for the preparation of magnets in refrigerator doors and the like, a substantially higher intensity of magnetization is obtainable in the magnets formed from such oxides which are ground for substantial periods beyond the point where any appreciable reduction in particle size occurs. In the case of metal powders, such as those of cobalt, chromium and nickel, and in mixtures comprising cobalt and nickel, structures are obtained in the agglomerates which permit pressing of the thus ground powders into a relatively strong shaped mass, which retains shape after the pressure is removed and during the sintering process outside of a mold. This also occurs in various mixtures comprising two or more of nickel, cobalt, iron and manganese, with or without grain-refining ingredients. These unique properties, however, are found not to occur when the grinding takes place in the presence of a continuous phase of liquid.

In the modification of FIGS. **9** and **10** the container is completely lined with a flexible rubber-like material which may be adhered to the rigid wall and bottom portions over the entire rubber-metal interface. Means is also provided for forced or external circulation of both the grinding media and process material from peripheral portions, back to the central area. I have found that caking of process material during dry grinding is effectively prevented by making the surfaces **21** and **23** of the physical characteristics of a soft rubber. The resilience and deflection of such materials is such that build up of caked material is prevented.

Suitable lining materials depend obviously both on abrasion resistance and on grinding conditions. In the dry grinding of inorganic solids a tire-tread type compound of natural or synthetic rubber including neoprene and the rubber polymers of the diolifines, butadiene and isoprene such as polybutadiene, polyisoprene, copolymers of butadiene with one or more of the monoolefinic compounds of styrene, acrylonitrile, methylmethacrylate, propylene, etc. When a liquid is present during grinding, the liner should be one selected to be substantially non-swellable in the liquid as abrasion resistance is found to be generally drastically reduced in accordance with swellability. The circulation of the process material through the agitated grinding media is important both on speed of grinding and on particle size distribution. A more uniform particle size is obtained with improved circulation. When the natural internal circulation is insufficient external or forced circulation is required.

The natural circulation is dependent on aspect ratio, (R) i.e. the ratio of depth to diameter of the bed of agitated media, about optimum natural internal circulation is obtained with a ratio of container depth to diameter of about one or a ratio of depth of bed to diameter of about one-half. In FIG. **11**, I have illustrated schematically, the influence of aspect ratio on various factors including relative ease of natural circulation (shown by the dotted curve, **80**); relative ball pressure shown by relative lengths of the arrows **81**, **82**, **83**, and **84** for the apparatus A, B, C, and D, illustrated above. As seen from FIG. **11** when the depth of bed to diameter of bed (aspect ratio — R) ratio — is about one-fourth to about one-twentieth external circulation is not essential but is desirable, particularly when the aspect ratio, R, is less than one-tenth. When the aspect ratio is greater than two then circulation is essential but

ball pressure is too high for most advantages obtained by dry grinding. When the aspect ratio is greater than one-twentieth dry grinding is not practicable without forced circulation.

Referring further to the modification in FIGS. **9** and **10**, the means for providing forced or external circulation of both the agitated grinding media and the process material comprises one or preferably two or more circumferentially spaced peripheral ports **70** connected to a conduit **71** which run between the ports **70** and the suction side of a fluid operated diaphragm pump **72**. The discharge end of each of the pumps **72** is connected to a conduit **73** which runs between the pumps **72** and a central portion of the container **2**, so that discharge of both grinding media and the process material from the pumps occurs near the axis of the container. The flow of material is due both to centrifugal forces exerted because of the arms **11** and the pump means **72**. While diaphragm pumps **72** operate most satisfactorily when there is a continuum of liquid in the container (which liquid may or may not be present) they are also operative with non-packing round balls in the absence of liquid continuum (i.e. a continuous phase of liquid).

It is also apparent that in accordance with the provisions of the patent statutes, modifications of the invention may be made without changing the spirit thereof.

Having described my invention, I claim:

1. In apparatus suitable for the dry grinding and reacting of inorganic solids, which apparatus comprises a vertically disposed, generally cylindrical container having a generally cylindrical sidewall and a bottom connected around the periphery to said sidewall, an agitator having a vertical shaft portion and at least one pair of oppositely extending rigid arms rigidly connected to said shaft, each of the arms of said pair extending outwardly toward said cylindrical wall and the outer end thereof being spaced from the inner surface of said wall, the lowermost pair of said arms being spaced from said bottom and each successive higher pair being vertically spaced from each lower pair, a bed of grinding media which consists essentially of a number of generally ball-like unconnected and freely movable elements disposed in said container over said bottom and having a depth sufficient to overlie and envelop opposite coplanar portions of the lowermost pair of said arms, and, means for rotating said shaft of said agitator to cause said arms enveloped by said grinding media to rotationally move through said bed of grinding media and at a sufficient speed to cause said bed to assume an apparent volume during said rotation that is substantially greater than in the unagitated state; the improvement which comprises proportioning said container to provide a ratio of depth of sidewall to diameter of from one-half to one-tenth and providing a bed of grinding media having a flat bed depth to diameter ratio of one-fourth to one-twentieth.

2. The apparatus of claim **1** wherein the arms of the lowermost pair of arms extend radially outwardly from said shaft in the same horizontal plane.

3. The apparatus of claim **1** wherein the ratio of said wall accumulation to diameter agglomerates one-fifth to one-sixth.

4. The apparatus of claim **1** having means for the prevention of accummulation of caked agglomerates of partly dry ground process material on the bottom of said container.

5. The apparatus of claim **4** wherein said means for prevention of accumulation of agglomerates comprises a screen having openings smaller in size than said elements of grinding media and means for continuously collecting partly processed material passing through said screen, and means for returning collected material to the action of the agitated grinding media.

6. The apparatus of claim **4** wherein said means for prevention of accumulation of caked agglomerates comprises means for vibrating said bottom of said container.

7. The apparatus of claim **6** wherein said vibration of said bottom is fluid actuated.

8. The apparatus of claim **1** wherein said bottom is flexibly attached to the said cylindrical side wall and means is provided for this purpose.

9. A method of dry grinding inorganic solids of a granular or particulate nature to produce smaller particle size and selective structural changes which comprises adding solids to be processed in the absence of a continuous phase of liquid to a bed of grinding media comprising essentially a plurality of freely moveable ball-like elements which in the unagitated condition forms a relatively flat bed having a thickness to diameter ratio of one-fourth to one-twentieth and which is maintained in circular peripheral form, continuously moving a horizontally disposed rigid bar through said bed of grinding media and material in process at a speed sufficient to cause a substantial increase in the total apparent volume of the grinding media and material in process so that in the agitated condition the said total volume is greater than that in the unagitated condition whereby the mean free paths between grinding elements is increased with resultant increase in the velocities when peening impact is had on said material being processed.

10. The method of claim **9** wherein grinding elements in said bed consist essentially of hard dense ball-like solids having a diameter of less than one-half inch and where said apparent increases in volume caused by agitation is at least 20 percent of the normal unagitated volume.

11. The method of claim **9** wherein the weight of the material to be processed and within the bed of grinding media is about one-fifth to one twenty-fifth the weight of the grinding media.

12. The method of claim **11** wherein caked agglomerates of partially ground material in process are automatically removed from surface and returned to the agitated bed of grinding media.

13. The method of claim **11** wherein the grinding time is continued for a substantial time after substantial minimum particle size is obtained, whereby changes in properties of ground particles occur.

14. Apparatus according to claim **4** wherein said means for prevention of caked agglomerates is a layer of resilient rubber-like material.

15. Apparatus according to claim **4** wherein both the bottom and wall portions contact the activated grinding media have a layer thereon of resilient rubber-like material.

16. A method of grinding of solid substances which comprises adding the relatively coarse solids to be processed to a bed of ball-like elements which bed in the unagitated state has a ball pressure at the bottom thereof of 200 to 1,200 grams per square centimeter, said ball pressure being the weight of a vertical column of the said ball-like elements of 1 square centimeter in cross section and of a height equal to the depth of said bed less the weight of a similar column of any continuous phase of liquid in which said ball-like elements are immersed, continuously moving a horizontally disposed rigid bar through said bed near the bottom thereof at a speed to cause a substantial increase in the apparent volume of the total of grinding media and process material whereby the mean free path, between elements of grinding media is increased with resultant increase in momentum of individual elements when peening impact is had on the material in process.

17. The method according to claim **16** wherein both agitated media and material in process is circulated from peripheral portions of said bed to the central area thereof and then radially out from the central area to said peripheral portions, whereby a more uniform particle size is obtained.

18. The method according to claim **16** wherein there is an absence of a continuous phase of liquid in said agitated bed of grinding media and material in process.

19. The method of claim **17** wherein there is a continuous liquid phase in said bed of agitated media.

20. The method of claim **17** wherein the material in process is successively ground in beds of agitated grinding media having ball-like elements of substantially different diameters, the second bed having elements of substantially smaller diameter than the first.

21. The method according to claim 16 wherein the grinding occurs in the absence of a continuous liquid phase, but in an atmosphere of a gas that is inert under grinding conditions to the solids being ground.

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