

[54] METHOD FOR REACTING MATERIALS

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Related U.S. Application Data

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1970, Pat. No. 3,670,970.

[52] U.S. Cl. 241/27

[51] Int. Cl. B02c 19/00

[58] Field of Search 241/27

[56] References Cited

UNITED STATES PATENTS

3,024,092 3/1962 Gessler 241/27 X
3,238,049 3/1966 Somers 241/27 X

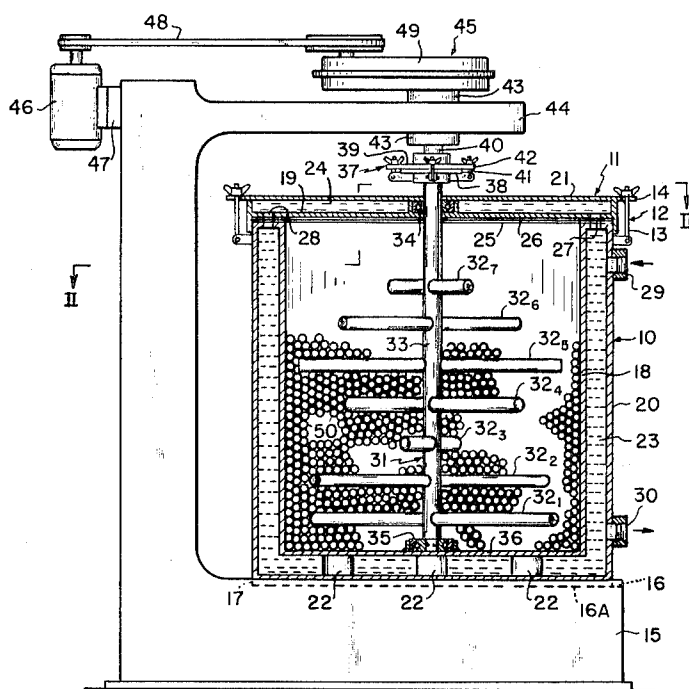
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[57]

ABSTRACT

Inorganic materials with unique chemical and/or physico-chemical properties are obtained by subjecting mixtures of reactants such as metal and ceramic powders and other particulate materials to attritive action. The reactants are activated by mechanical means by highly energized attritive action and reacted either simultaneously or in substantial part thereafter. In some embodiments a liquid continuum may be present, while in other embodiments the absence of a liquid continuum is preferred. The attritive action is preferably continued for a substantial time after a minimum particle size is attained. Further, means are provided in the attritor apparatus to decrease or prevent caking of solid materials in the bottom of the apparatus.

4 Claims, 10 Drawing Figures



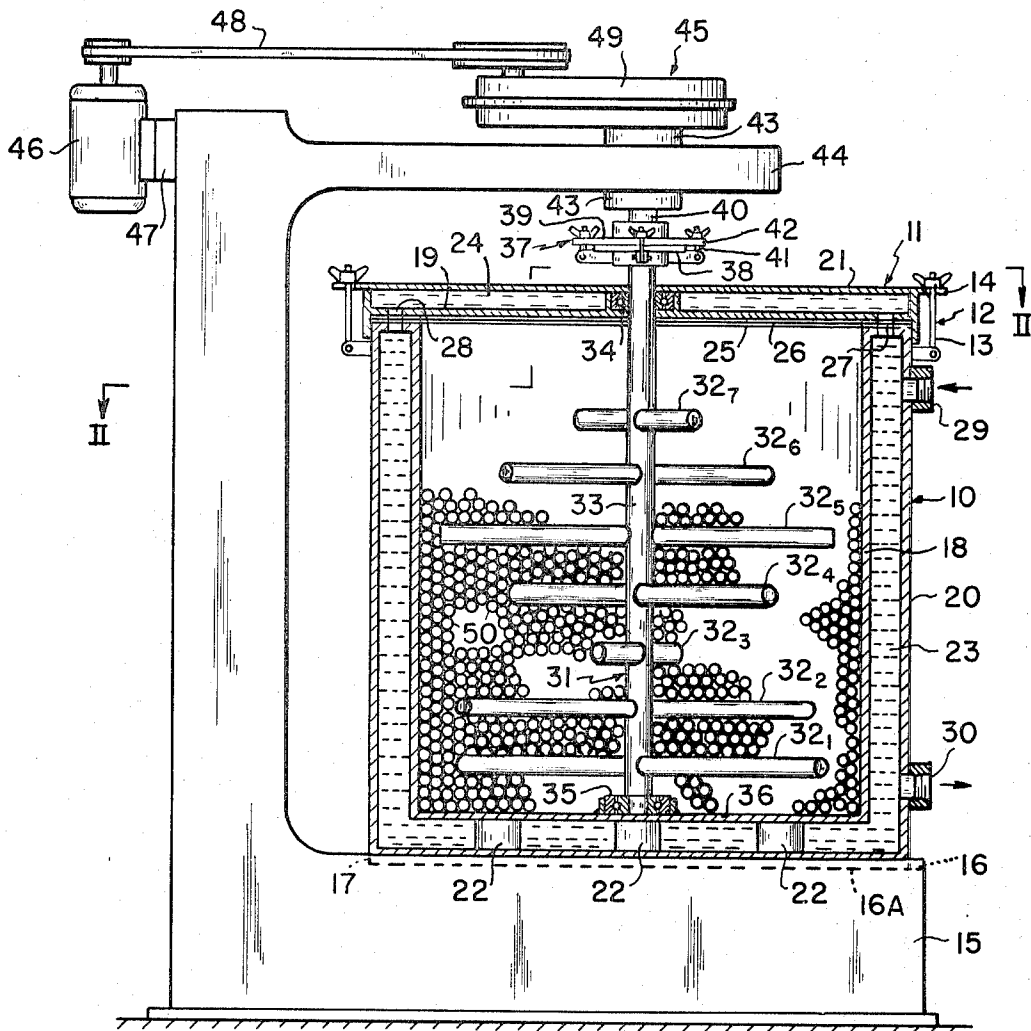


Fig. 1

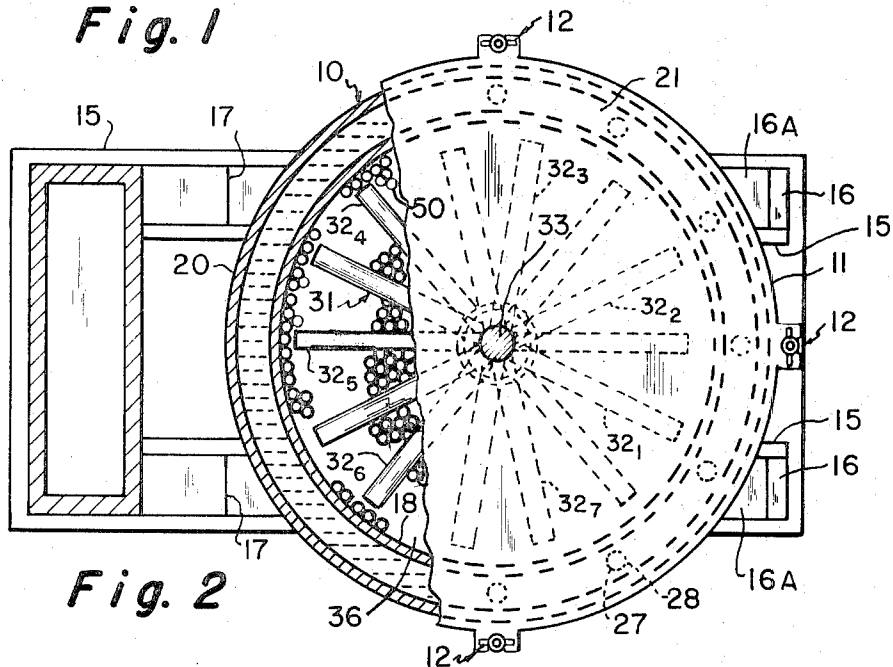


Fig. 2

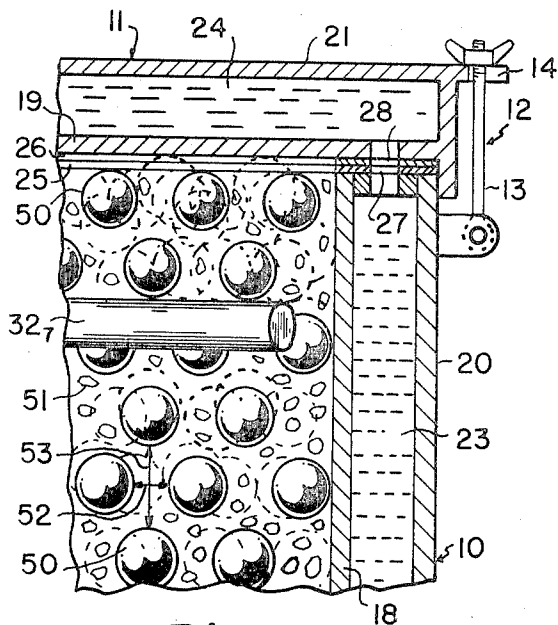


Fig. 3

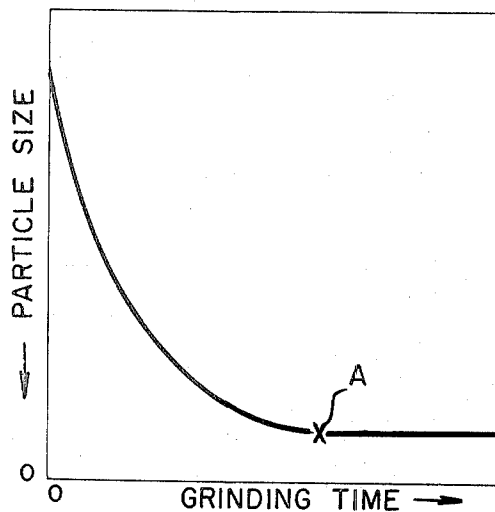


Fig. 6

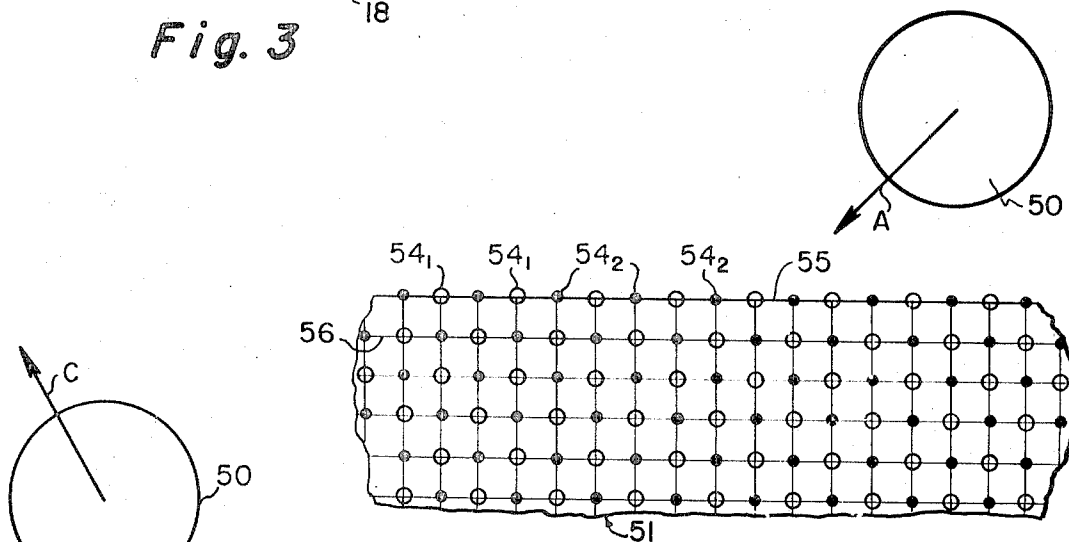


Fig. 4

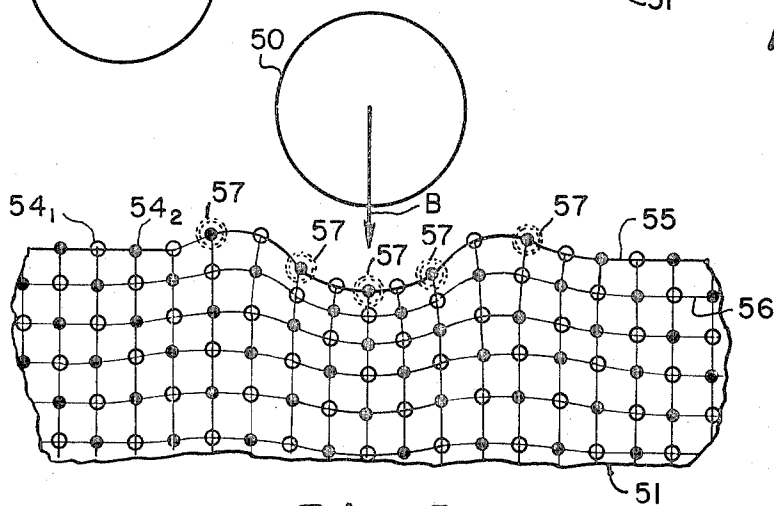


Fig. 5

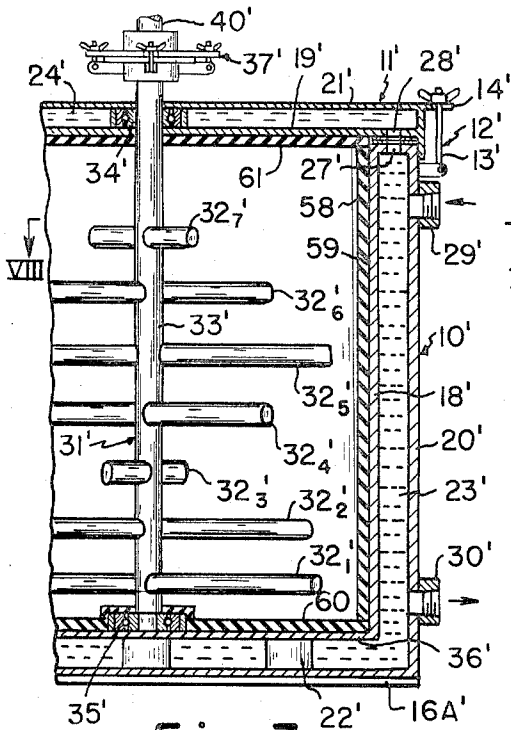


Fig. 7

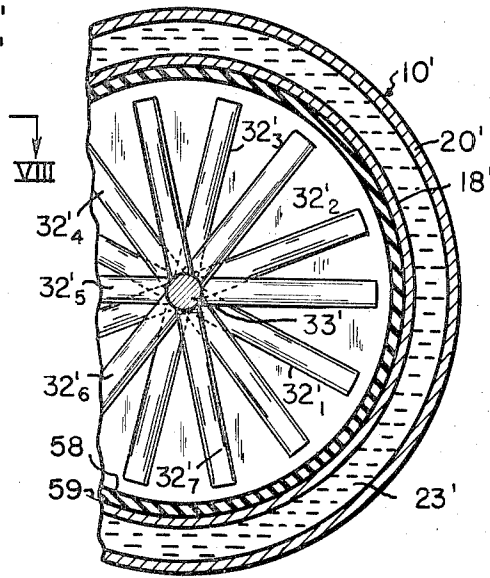


Fig. 8

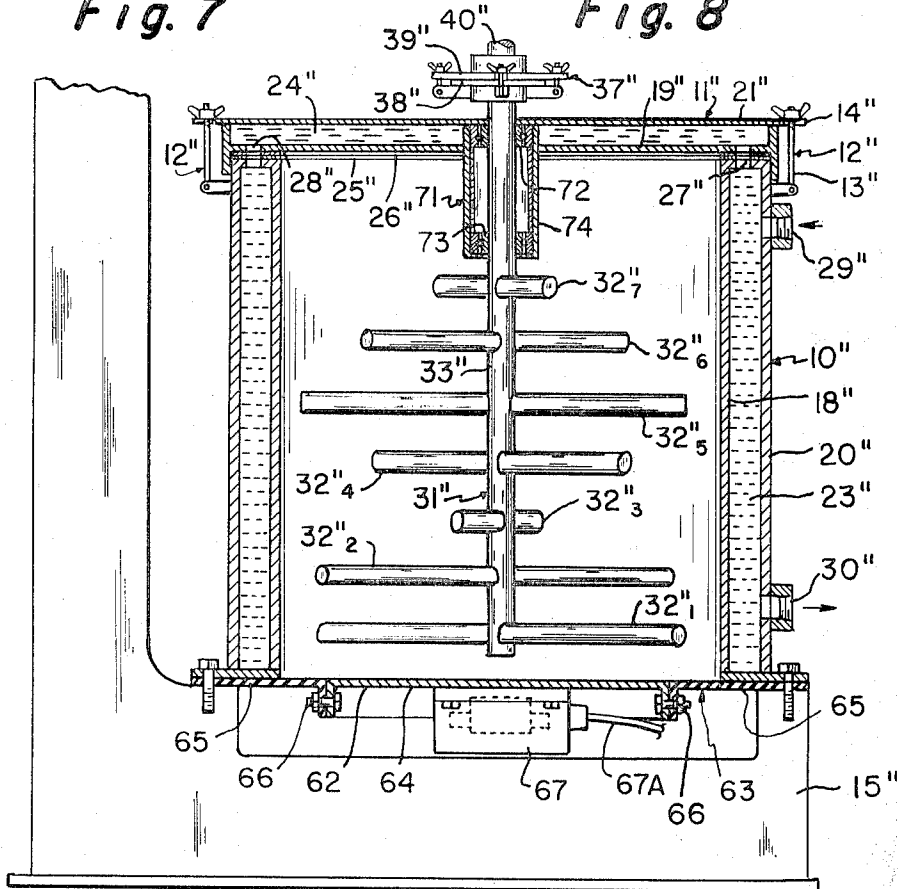


Fig. 9

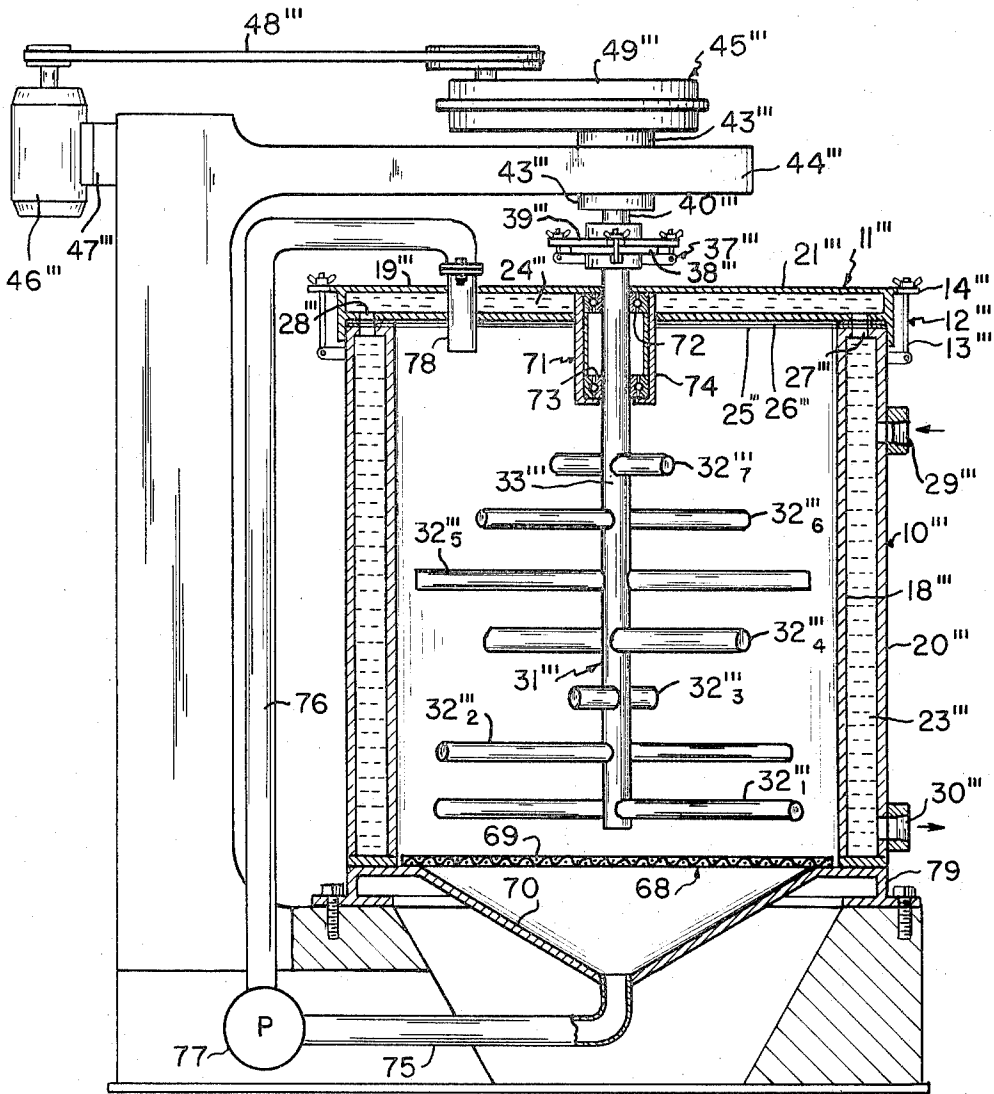


Fig. 10

METHOD FOR REACTING MATERIALS

RELATED APPLICATIONS

This application is a continuation-in-part of application Ser. No. 081,811, filed Oct. 19, 1970 and issued as U.S. Pat. No. 3,670,970, June 20, 1972.

FIELD OF THE INVENTION

This invention relates to attritors and particularly the activation of materials in attritors.

BACKGROUND OF THE INVENTION

Chemical and physico-chemical reactions have been known to occur only under certain conditions. For example, coal and air are known to interact only on the application of heat. This is because the materials must be placed in an unstable or reactive state usually by placing the electrons of the respective materials in high energy states. The ways generally used to react materials have been heat, pressure and/or catalysts. It has not been suggested that chemical and physico-chemical reactions could be initiated or performed by purely mechanical means.

Attritors have been known and used for years. Exemplary of the art are U.S. Pat. Nos. 2,764,359, 3,131,875 and 3,149,789 and British Pat. No. 716,361. Attritors have been used to reduce particulate materials to very fine particle size (e.g., 30 microns or less). Balls, pebbles, beads and the like of steel, glass, ceramic, stone, coral, tungsten carbide, titanium dioxide, sillimanite and the like, typically having a 10 mesh to ¼ inch diameter, are used as the attritive elements or grinding media. The attritor elements are placed and then kept in constant motion by an agitator having blades rotating horizontally through the elements typically at between 75 and 600 rpm. While it has been suggested that the attritor action can be performed without a liquid continuum, it has been typical to comminute in an attritor in the presence of a liquid. Thus, attritors have been used for grinding tungsten carbide, paint pigments, coal, procaine penicillin and a myriad of other materials.

One of the primary problems with dry conditions is that kinematic movement of the attritor elements near the bottom of the attritor vessel is not maintained. As a result, a hard layer or crust of from 1/32 to ¼ inch in thickness usually builds up on the bottom substantially reducing the amount of material which is comminuted. Further the hard crust is difficult to remove, usually requiring chiseling to break up. For this reason, the attritor action has been normally carried out in a liquid continuum. The liquid continuum also facilitates handling of the material into and out of the apparatus.

It has been proposed to perform chemical reactions involving organic materials in attritors; see U.S. Pat. No. 3,149,789. Specifically, certain types of polymerization are carried out in attritors to produce elastomers or other resins with more uniform polymeric chain lengths. The mechanism for performance of these attritive reactions has not been suggested. Nor has it been suggested that attritive action can be adapted to react and initiate the reaction of materials simply by mechanical means.

The present invention provides a wholly new and surprising way of producing materials with unique chemical and physico-chemical properties. It provides a way of producing known and unknown compositions by me-

chanical means without the presence of heat, pressure and/or a catalyst. In addition, it provides means for performance of comminutions and reactions in attritors in the absence of a liquid continuum without involving the formation of a hard-pan or crust layer at the bottom of the attritor vessel.

SUMMARY OF THE INVENTION

Materials with unique chemical and physical properties are formed from a plurality of reactants by mechanical means by attritive action. The mechanical means may be the sole means for activation. The reactants are distinct inorganic particulate or granular materials such as different metal or ceramic powders. For example, mixtures of two or more metal powders such as molybdenum, nickel, chromium, cobalt, aluminum and/or iron; and a mixture of ceramic powders of silica, feldspar, clay and limestone. The formation of the unique materials from the activated reactants is performed in some embodiments simultaneously with the attrition or in some embodiments in substantial part subsequent to completion of attrition. In either instance, the unique materials are made by disposing the reactants in an attritor and agitating or dispersing the reactants by attritive action. Simultaneously, the reactants are activated by attritive action and react to form materials with different properties from the reactants. For example, attrited mixtures of metal powder produce powdered alloys that permit the molding of the various products by well-known sintering processes with high strength properties at high temperature (e.g., 2,000° F). And attrited mixtures of silica, feldspar, clay and limestone powders produces on firing a porcelain with higher compressive loading properties.

Preferably the attritive action is performed in the absence of a liquid continuum in certain embodiments of the invention. In such dry conditions, the attritive action re-assembles kinematically the classic model of an ideal gas. The energy imparted to the reactants is a function of the relative velocities of the attritor elements (e.g., the balls) and the reactants, their relative masses, and the number of collisions (i.e., points of contact) involving elements and material.

The mechanical energy of activation is imparted by rotating the agitator of the attritor at relatively high speed (usually between 100 to 700 rpm but possibly as high as 1,400 rpm) so that the attritor elements are continuously maintained in a state of high relative motion. The material is activated by its presence at the collision between attritor elements or between attritor elements and the surfaces of the attritor vessel. The process is statistical and time dependent. Therefore to attain activating energy, the attritive elements must have high velocity and random motion with high kinetic energy.

Preferably, the material is also comminuted by the attritive action. New surfaces are thereby exposed which are readily activated so that the reactivity can be increased. In addition, it is preferred that attritive action be continued for a substantial length of time after there is no substantial mean decrease in particle size, i.e., after the comminution of the reactants is substantially completed. Where comminution is "completed," subdivision of the particles may occur, but the rate of subdivision and the rate of cohesion are substantially equal so that an equilibrium condition is present.

With dry conditions, it is also preferred that the attritor apparatus have means to decrease or eliminate caking or crusting of the solid material adjacent bottom surfaces of the attritor. Such means may be provided by a resilient layer positioned adjoining the bottom surface of the attritor and preferably bonded thereto preferably during or after polymerization and/or curing of the resilient material. Alternatively, such means may be provided by vibratory means positioned adjacent the bottom, or by a perforated bottom preferably through which a vacuum is drawn on the material.

Other details, objects and advantages of the invention will become apparent as the following description of the present preferred embodiments and the present preferred methods of practicing the same proceeds.

BRIEF DESCRIPTION OF THE DRAWINGS

In the accompanying drawings is shown present preferred embodiments of the invention and is illustrated present preferred methods of practicing the same in which:

FIG. 1 is an elevational view with portions broken away of an attritor suitable for practice of the present invention;

FIG. 2 is a cross-sectional view taken along line II—II of FIG. 1;

FIG. 3 is a fragmentary elevational view in cross-section showing a portion of the attritor of FIG. 1 during attritive action;

FIGS. 4 and 5 are schematics illustrating activation of the material by attritive action;

FIG. 6 is a graph illustrating the relation between particle size of the material and time during the performance of chemical and physico-chemical reaction by attritive action;

FIG. 7 is a fragmentary elevational view in cross-section of an alternative attritor in accordance with and suitable for the present invention;

FIG. 8 is a fragmentary top view in cross-section of the attritor shown in FIG. 7;

FIG. 9 is a fragmentary elevational view with portions broken away of a second alternative attritor in accordance with and suitable for the present invention; and

FIG. 10 is an elevational view with portions broken away of a third alternative attritor in accordance with an suitable for the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring to FIGS. 1 and 2, a cylindrical attritor vessel 10 is provided with a cover 11. The capacity of the vessel will vary from 1 gallon for an experimental attritor to several hundred gallons for commercial production. Cover 11 is fastened to vessel 10 by fastening assemblies 12 positioned in quadrature around the periphery of the vessel and cover. Each assembly 12 includes a pivoted screwdown 13 attached to vessel 10, and a bifurcated member 14 attached to cover 11 to receive screwdown 13. By assemblies 12, the cover can be removed from the vessel for charging and discharging of the vessel. Preferably, an access port (not shown) may be provided in addition in cover 11 to provide for charging of the attritor apparatus without removal of the cover.

Vessel 10 is supported by base 15 having a pair of underlying supports having rails 16 along their lengths

with stops 17 at one end. Attached to the bottom of vessel 10 are slides 16A which are received into rails 16. By this arrangement, the attritor vessel can be discharged and recharged and thereafter positioned on base 15 for resumption of attritive action. Alternatively or supplementally, a discharge valve (not shown) may be provided in the bottom of the vessel 10 so that the attritor can be discharged without removal of vessel 10 from the base. This discharge valve can be installed for handling only the activated material in which instance it has a built-in screen to retain the attritive elements; the discharge valve can also be built without a retaining screen to permit discharge of the attritive elements.

Both vessel 10 and cover 11 have a double jacket to provide for cooling of the attritor during operation. Vessel 10 has inner liner 18 and outer liner 20 spaced away by their relative diameters and spacers 22 to provide space 23 for coolant within vessel 10. Similarly cover 11 has inner liner 19 and outer liner 21 spaced away and attached at their peripheries to provide space 24 for coolant within cover 11. The spaces 23 and 24 are joined by coinciding openings 27 and 28 in the vessel and the cover, respectively, and are sealed by coinciding gaskets 25 and 26, respectively, so that the vessel and cover are part of the same cooling system. Coolant may be supplied to the system through inlet port 29 and is discharged from the system through outlet port 30, or vice versa. Alternatively, the cooling system for the vessel may be independent of the cooling system for the cover, with each system having its own inlet and outlet ports. This assembly is preferred where it is desired to frequently remove and replace the cover from and to a sealed condition, e.g., where the activation and reaction as subsequently described are performed simultaneously in an inert atmosphere at about 18 to 20 psi. In some instances, it may be alternatively preferred that the cover not be cooled; in such instances, it is preferred that the cover be made in two semi-circular parts split to permit rapid removal from around the agitator assembly 31 hereafter described.

Vessel 10 is fitted with agitator assembly 31 having an agitator shaft 33 aligned coaxially within the vessel and agitator arms or blades 32_n extending symmetrically and horizontally from shaft 33. Shaft 33 is supported vertically by bearing means 34 and 35 positioned coaxially in cover 11 and vessel 10, respectively; alternatively, it may in some circumstances be appropriate to replace bearing means 34 with a simple seal. In any case, the agitator arms 32_n are distributed evenly throughout the length of shaft 33 within vessel 10 with the lowermost arms 32₁ spaced from the bottom 36 of the vessel to prevent jamming of attritive elements therebetween. The outer ends of arms 32_n are spaced from the internal sidewalls of the vessel to prevent jamming of attritor elements in that space, typically about 3/4 inch (i.e., at least two to three times the typical attritor element diameter). The arms 32_n in addition are preferably arranged with adjacent arms at an angle and with each successively higher arm trailing the adjacent lower arm; by this arrangement, the arms provide lift to the attritive elements so that the kinematics during attritor operation more closely approach the kinematics of an ideal gas where the motion is totally random.

The shaft of agitator assembly 31 extends through the cover 11 and terminates with assembly 37. Assembly 37 provides for the removal of the attritor vessel to charge and discharge the contents. Assembly 37 in-

cludes circular end plate 38 rigidly fastened to end portions of agitator shaft 33 and an abutting circular end plate 39 rigidly fastened to drive shaft 40. Drive shaft 40 is supported through bearing means 43 by support 44 integral with base 15. Fastened to end plate 38 is pivoted coupling members 41 in quadrature around its periphery, and fastened to end plate 39 is bifurcated member 42 in quadrature around its periphery to receive coupling 41. Assembly 37 is thus disassembled for removal of vessel 10 by detachment of coupling members 41 from bifurcated members 42. In some instances it may be necessary or appropriate to provide assembly 37 in which instance drive shaft 40 is simply an extension of agitator shaft 33, and bearing means 35 need not be used.

Agitator assembly is driven at high speed, usually between 100 to 700 rpm, but possibly as high as 1,400 rpm and above, by drive assembly 45. Drive assembly 45 comprises an electric motor 46 fastened to support 44 at 47, a V-belt pulley assembly 48, and gear reducer 49. The gear reducer is also supported by support 44 and is attached directly to drive shaft 40 to supply power.

The attritor apparatus is completed by attritor elements 50 disposed within vessel 10. They may be balls of, for example, high carbon steel, tungsten carbide, or ceramic, or they may be pebbles formed naturally. They preferably have high specific gravity so to provide high momentum and high kinetic energy when they collide with each other to activate the constituent materials or reactants 51. The size of the attritor elements 50 will preferably vary between 1/32 and 1/2 inch in diameter and will typically be between 1/4 and 3/16 inch in diameter; smaller elements, although available, are not deemed to provide sufficient mass to provide the high kinetic energy needed to activate the material 51. The optimum size of the attritor elements will depend on the size of vessel 10, the properties (e.g., hardness) of the material 51 being reacted, and the speed of rotation of the agitator assembly. The ratio of attritive elements 50 to internal volume will depend on whether the attritive action is in the presence or absence of a liquid continuum. Typically, in the presence of a liquid continuum, the volume of the attritive elements will extend to cover most if not all of the agitator arms 32, while in the absence of a liquid continuum, the volume of the attritive elements is about 1/2 to 3/4 of the closed volume of the attritor vessel.

Referring to FIG. 3, the attritive action is provided by elements 50 during rotation of the agitator assembly 31 as shown. Elements 50 are in a highly energized state exhibiting omnidirectional or random motion with coordinate components as demonstrated by 52 and 53. Material 51 is shown interspersed between elements 50, and the dynamics of elements are illustrated in dotted outlines. This illustrated highly energized state enables the attritor elements 50 to mechanically impart the necessary activating energy to the material 51 to increase energy of atoms thereof and enable them to react with other reactants.

The microscopic impingement of the elements 50 on the material 51 is schematically shown by FIGS. 4 and 5. Material 51 is shown having atoms 54, and 54₂ of different elements in an atomic lattice 56 with surface 55. Element 50 moves in the direction shown by arrow A to impingement on the surface 55 of the material which is already in contact with another element 50 or an in-

ternal surface of vessel 10 (not shown). When element 50 strikes the surface 55 of material 51 as shown by arrow B, it imparts activating energy by distorting lattice 56 and by moving electrons of surface atoms 57 into high energy states. Atoms 57 are thus available to react with different reactant material and form different material with properties different from the reactants.

The particle size of material 51 will vary with the reactants, the parameters of the attritor, and the rate of reaction desired. The particle size may vary from particles measuring as little as about 50 microns in diameter or even less to as large as 1/8 inch in diameter and even greater. The particle size is not considered limiting. Preferably, the reactants are comminuted during the activation, decreasing particle size and increasing reactivity as previously explained. Therefore the particle size of the reacted material will typically range from 25 microns to 0.5 microns depending on the material properties and the length of the attrition.

Referring to FIG. 6, it is thus preferred that the attritive action be continued for a substantial time after a minimum mean particle size is attained. Point A is illustrative of the point in time where comminution of the reactants and newly formed material is substantially completed. Point A is called hereafter the "comminution cut-off time." Comminution of the material beyond that point in time is substantially balanced by the cohesion which occurs in the material as shown. The attritor operation would be terminated at this point in the simple prior art grinding or comminution.

Surprisingly, it has been found, however, that subjecting the reactants to attritive action beyond the comminution cut-off time results in production of materials with unique properties. For example, attrition of mixtures of two or more metal powders such as nickel, chromium, cobalt and/or iron substantially beyond the comminution cut-off time, preferably one-half hour or longer, produces alloys with unique structural properties — some alloys of which cannot be made by conventional alloying techniques. These attrited powder alloys permit the molding of various products by well-known sintering processes with high strength properties even at high temperatures (e.g., 2,000° F.)

In such reactions, the activation and reaction of the reactant materials by attritive action results in a material having a crystal structure with unique properties. Because of the high energy imparted by attritive action, it is believed that selective cohesion at certain crystal planes results in structure-oriented solids with unique properties. However, whatever the mechanism, the unique properties are not found in comparable materials which have been typically comminuted in accordance with prior art practice in a liquid continuum.

Other details, objects and advantages of my invention will be apparent from the non-limiting examples.

EXAMPLE I

Porcelain was made by forming a standard slip or aqueous slurry of silica, feldspar, clay and limestone. Three runs were made in a one gallon attritor designated No. 1-S Attritor and available from Union Process Co., 1925 Akron Peninsula Road, Akron, Ohio. The runs were all performed with 1/4 to 3/8 inch diameter flint stones as the attritive elements. The runs varied in time as tabulated below.

Test units were made from the attrited slurry by firing in accordance with the standard procedures and the physical properties measured. The results are shown in TABLE I.

TABLE I

Run No.	Time of Attritor Run in Minutes	No. of Units Tested	Compressive Load at Rupture	
			Average p.s.i.	Standard Deviation p.s.i.
1	90	15	13,100	450
2	150	15	14,050	945
3	240	14	14,550	740

In each instance the compressive load at rupture was higher than ceramics of the same composition prepared by standard processing without subjection to attritive action (i.e., 1,200 psi). In addition, shrinkage of the units during firing was observed to be greater than with standard prepared porcelain of the same recipe. This indicated an unusually fast progress of sintering and that the firing could be performed at lower temperatures than with standard porcelain making procedures.

Subsequently compositions were prepared in which the silica, feldspar or clay was individually subjected to attritive action before formation of the slip. It was found on preparation and firing of test units that the unique materials were observed when the silica or feldspar were the only material attrited, but not when the clay was the only material attrited.

EXAMPLE II

Metal alloys were made by forming a dry mixture of nickel powder and alumina abrasive powder (i.e., Al_2O_3). The formulation was 13 pounds of nickel powder and 0.26 pounds of alumina powder (2 percent by weight) pre-mixed in a plastic bag.

The formulation was subjected to attritive action in a No. 10-S attritor of Union Process Co. The attritor was equipped with cooling jackets, unjacketed pressure sealed cover, and bottom discharge valve. The attritor had four standard type arms (two top arm plugged). The attritive elements were $\frac{1}{4}$ inch diameter carbon steel balls filled to the top arms of the agitator (i.e., 200 pounds). The attrition was performed in an argon atmosphere at about 4 pounds above atmospheric pressure.

The attrition was carried on for 40 hours at about 125 rpm in the absence of a liquid continuum. 50-100 gram samples were taken at 0, $3\frac{1}{2}$, $6\frac{1}{2}$, $20\frac{1}{2}$, 26, $30\frac{1}{2}$ and 40 hours. The temperature of the material at discharge was $145^\circ F$.

The samples taken at $3\frac{1}{2}$ and 40 hours were examined under a microscope (x680). In both samples the particles increased and then decreased in size as follows: (i) small fraction 1-3 (unattrited) to 1-4 ($3\frac{1}{2}$ hours) to 1-2 microns (40 hours); (ii) majority 4-7 (unattrited) to 5-10 ($3\frac{1}{2}$ hours) to 3-7 microns (40 hours); (iii) large fraction 8-14 (unattrited) to 11-20 ($3\frac{1}{2}$ hours) to 8-14 microns (40 hours); (iv) few 15-30 (unattrited) to 21-50 ($3\frac{1}{2}$ hours) to 20-280 microns (40 hours); and (v) included to 70 (unattrited) to 80-140+ microns ($3\frac{1}{2}$ hours) to not observed at (40 hours). The large particles showed the formation of layers different from the charged material at both $3\frac{1}{2}$ and 40 hours. A $\frac{1}{2}$ ounce sample of the discharge (i.e., 40 hour) material was retained in the laboratory.

EXAMPLE III

Metal alloy was made by attritive action from a dry mixture of nickel powder, molybdenum powder and alumina abrasive powder (i.e., Al_2O_3). The formulation was 11 pounds of nickel (85 percent by weight), 2 pounds of molybdenum (15 percent by weight) and 0.26 pounds of alumina (2 percent by weight). The metal powders were premixed in a plastic bag.

The formulation was subjected to attritive action in a No. 10-S attritor of Union Process Co. using a No. 15-S attritor frame and motor drive. The attritor was equipped with a cooling jacket, unjacketed pressure sealed cover, and bottom discharge valve. The attritor had four standard type arms (two top arms plugged). The attritive elements were $\frac{1}{4}$ inch diameter carbon steel balls filled to the top arms of the agitator (i.e., 220 pounds). The attrition was performed in a nitrogen atmosphere.

The attrition was carried on for 11 hours at about 125 rpm in the absence of a liquid continuum. Samples were taken at 6 hours and 11 hours. The samples taken at 6 hours and 11 hours were examined under a microscope. The particle sizes of the samples microscopically examined were as follows: (i) small fraction less than 4 (6 hours) to less than 4 microns (11 hours); (ii) majority 4-7 (6 hours) to 4.5-7 microns (11 hours); (iii) large fraction 8-18 (6 hours) to 8-15 microns (11 hours); (iv) few 20-35 (6 hours) to 18-70 microns (11 hours); and (v) included 36-112 (6 hours) to 28-210 microns (11 hours). In addition, it was observed (i) that the particles of the large fraction at 6 hours had no definite shape and evidenced breaking apart, (ii) that the particles of the few at 6 hours had shown breaking apart and layering, (iii) that the particles of the included at 6 hours had some layers and breaking apart, (iv) that the particles of the few at 11 hours had breaking and welding, and (v) that the particles of the included at 11 hours had layering and breaking apart.

EXAMPLE IV

Metal alloy made by attritive action from a mixture of iron powder, chromium powder, aluminum powder and alumina powder. The mixture was subjected to attritive action in the same attritor apparatus as used in Example III with an argon atmosphere.

The attrition was carried on for 40 hours at about 125 rpm in the absence of a liquid continuum. The discharge was compared with the unattrited mixture. The samples were examined under a microscope. The particle size of the samples examined were as follows: (i) majority 1-5 (unattrited) to 1-7 microns (40 hours); (ii) large fraction 6-14 (unattrited) to 8-21 microns (40 hours); (iii) few 15-30 (unattrited) to 22-42 microns (40 hours); (iv) included 35-84 (unattrited) to 42-70 with one 140 microns (40 hours).

EXAMPLE V

Metal alloy powder was made by attritive action from a dry mixture of iron powder, chromium powder, aluminum powder and alumina powder. The attritor apparatus used was the same as that described in connection with Example III with an argon atmosphere.

The attrition was carried on for 40 hours at about 125 rpm in the absence of a liquid continuum. Samples were taken at 0, 6, 11, 16, 30 and 40 hours. The samples taken at 0, 16, 30 and 40 hours were examined

under a microscope (x680). The particle sizes of the samples varied as follows: (i) small fraction 1-3 (unattrited) to less than 4 (16 hours) to less than 4 (30 hours) to 1-7 microns (40 hours); (ii) majority 4-7 (unattrited) to 4-7 (16 hours) to 4-7 (30 hours) to 8-14 microns (40 hours); (iii) large fraction 8-20 (unattrited) to 8-20 (16 hours) to 8-21 (30 hours) to 15-35 microns (40 hours); (iv) several 20-60 microns (unattrited) to not observed in subsequent samples; and (v) few and included 70-140 (unattrited to 25-84 with one 130 (16 hours) to 25-100 with included 100-280 (30 hours) to 40-160 microns (40 hours). It was also observed (i) that the particles of the included at 16 hours had layers and were welded together, (ii) that the particles of the large fraction and included at 30 hours had layers and the same general shape, and (iii) that the particles of the few at 40 hours had layers.

In another aspect of the invention, means are provided to avoid caking of solid materials in the bottom of the attritor vessel during attritive action. The alternative embodiments contemplated for providing these means are shown in FIGS. 7 through 10 of the attached drawings and hereinafter described.

Referring to FIGS. 7 and 8, attritor apparatus is shown which has the same and alternative elements as shown in and described in connection with FIGS. 1 and 2. A resilient layer 58 is attached to the internal sidewalls 59 of cylindrical attritor vessel 10'. The resilient layer is preferably composed of a flexible resin or a rubber which is preferably bonded to the sidewalls 59 during polymerization and/or curing of the resin or rubber. Likewise, resilient layer 60 is attached to internal bottom surface 35' of vessel 10' and resilient layer 61 is attached to the inside of cover 11'.

By this arrangement, the entire internal surfaces of vessel 10' and cover 11' are covered with a resilient layer, albeit the layer 60 to bottom surface 35' is the only resilient means needed to avoid caking of solid material in the bottom of the attritor vessel. The purpose of covering all inside surfaces is that the amount of energy dissipated in the form of heat during attritive action by collision of the attritive elements with the surfaces of the attritor can be reduced. It should be noted, however, that although the resilient layer must have sufficient elasticity to avoid caking, it should also have sufficient hardness to permit high energy collisions involving attritive elements and reactants at the surfaces of the vessel.

Referring to FIG. 9, attritor apparatus is shown having an alternative embodiment of means to avoid caking of solid materials adjacent the bottom of the attritor vessel. The elements and alternatives are basically the same as those described in connection with FIGS. 1 and 2. The differences are that (1) a different bearing assembly 71 having a cylindrical housing 74 with bearing means 72 and 73 is used, (2) a cavity is provided in base 15'' to accommodate the different bottom assembly 63 and (3) the bottom assembly 63 of the vessel 10'' is unjacketed.

The anti-caking bottom assembly 63 is comprised of a rigid circular part 64 and a flexible annular part 65. Rigid part 64 is fastened to flexible part 65 by suitable fastening means such as a plurality of bolt assemblies 66, and the annular part 65 is in turn fastened to the sidewalls of vessel 10'' by suitable means as shown. Positioned adjoining rigid part 64 is vibratory means 67

powered by suitable means through connection 67A.

In operation, the vibratory means 67 is operated during the operation of the attritor apparatus. Vibratory means 67 causes the rigid part 64 and flexible part 65 to vibrate vertically to impart upward movement to attritive elements and material within the attritor apparatus and thereby avoiding the formation of caking adjacent the bottom of the vessel 10''.

Referring to FIG. 10, another attritor apparatus is shown having an alternative means to avoid caking of solid materials in the bottom of the attritor vessel. The elements and alternatives are again basically the same as that described in connection with FIGS. 1 and 2. The bearing assembly which supports agitator assembly 32''' is the same as that described in connection with FIG. 9. The base 15''' has cavities therein to accommodate the apparatus hereinafter described, and the bottom of vessel 10''' is unjacketed.

The anti-caking bottom assembly 68 is comprised of a perforated flat screen bottom 69 positioned above a conical bottom 70. The screen bottom 69 is supported at its periphery by conical bottom 70 which is in turn fastened at its periphery portions 79 to the sidewalls of vessel 10''' as shown. At the apex of the conical bottom is attached conveyor tube 75. Conveyor tube 75 is connected to the inlet of vacuum transporter or impeller 77, which is in turn connected at its outlet to conveyor tube 76. Conveyor tube 76 is connected at its opposite end through opening 78 in cover 11''' to the top internal portion of the attritor vessel.

In operation, the attritive elements are supported on screen bottom 69 and the material being processed is capable of falling through bottom 69. The material which enters the space between screen bottom 69 and conical bottom 70 is pulled by vacuum transporter or impeller 77 through conveyor tube 75 and subsequently pushed by vacuum transporter 77 through conveyor tube 76 to be resupplied to the apparatus for subsequent attritive action. In this way, the solid material cannot build up and crust on screen bottom 69 and caking adjacent the bottom of the vessel 10''' is avoided.

While the presently preferred embodiments of the invention have been specifically described, it is distinctly understood that the invention may be otherwise variously embodied and used within the scope of the following claims.

What is claimed is:

1. A method of forming an inorganic material having unique properties comprising the steps of:

A. forming a mixture of two or more powders selected from the group consisting of nickel, chromium, cobalt, iron, molybdenum, aluminum and alumina;

B. comminuting said mixture of powders by attritive action in the absence of a liquid continuum; and

C. continuing the attritive action for a substantial time after a minimum mean particle size is attained in said mixture to form an alloy powder with a crystal structure different from said mixture of powders.

2. A method of forming an inorganic material having unique properties as set forth in claim 1 wherein: step C is continued for a period of at least ½ hour.

3. A method of making porcelain having unique properties comprising the steps of:

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- A. forming an aqueous slurry of silica, feldspar, clay and limestone;
- B. comminuting said slurry by attritive action;
- C. removing substantial amounts of water from the attrited slurry; and

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- D. firing the attrited, water removed slurry.
- 4. A method of making porcelain having unique properties as set forth in claim 3 wherein: step B is continued for at least about 150 minutes.

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**UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION**

Patent No. 3,799,455 Dated March 26, 1974

Inventor(s) Andrew Szegvari

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 47, "an" should read --and--;

Column 7, line 44, "200" should read --220--;

Column 8, line 18, "preformed" should read
--performed--.

Signed and sealed this 2nd day of July 1974.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents