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Krekeler et al.

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[54] **HIGH SHEAR MIXING APPARATUS FOR MAKING SILICA GELS**

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[52] **U.S. Cl.** ....**23/285**, 23/283, 23/182 R, 261/84, 259/7, 259/8, 259/23, 259/24, 259/43, 259/44, 259/107, 259/108, 252/314, 252/359 R, 252/359 C

[51] **Int. Cl.** **C01b 33/16**, B01j 1/04, B01f 7/20

[58] **Field of Search**.23/283, 285, 252, 182 R, 270.5; 261/84; 259/7, 8, 23, 24, 43, 44, 107, 108; 252/359 R, 359 C, 314

[56] **References Cited**

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[57] **ABSTRACT**

Apparatus comprising a rotary agitator possessing movable sets of flat blades interspersed with stationary sets of flat blades, the pitch and clearances of the blades being such that high shear agitation is obtained. This apparatus is suitable for use in the carrying out of any process requiring high shear mixing. It has been found to be particularly useful in the preparation of silica gels of high quality.

11 Claims, 4 Drawing Figures

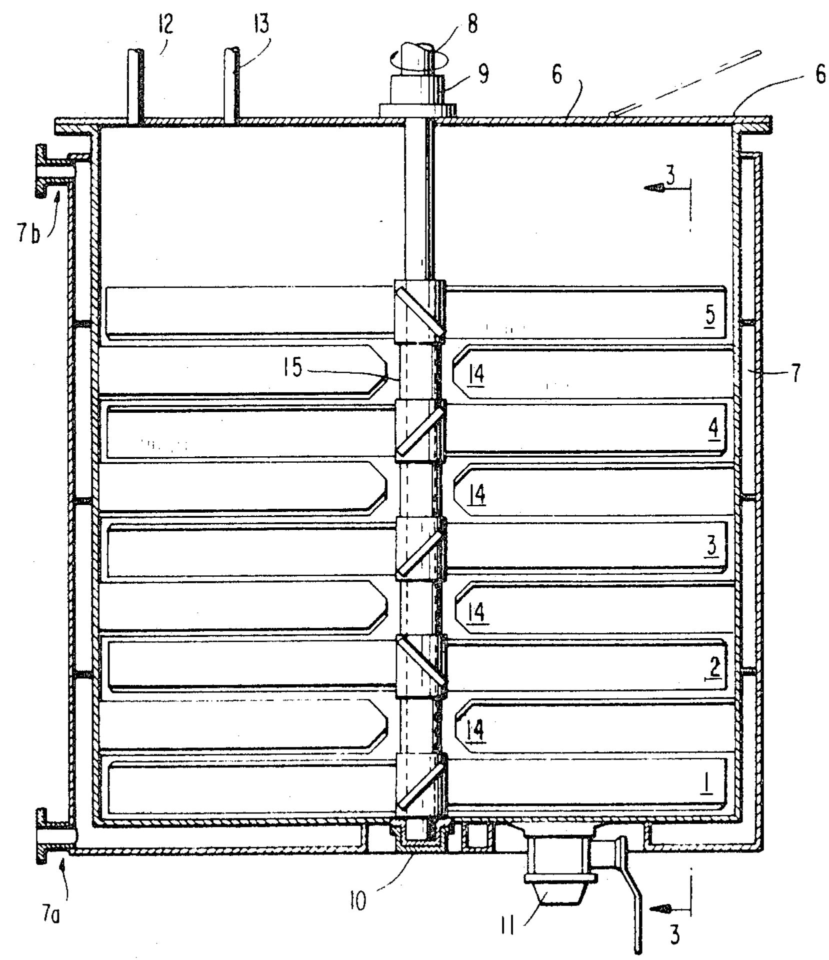


FIG. 1

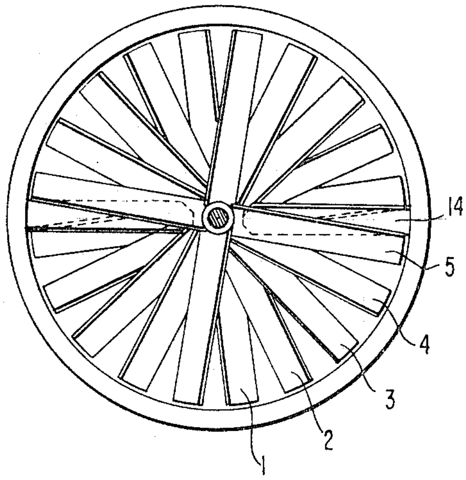
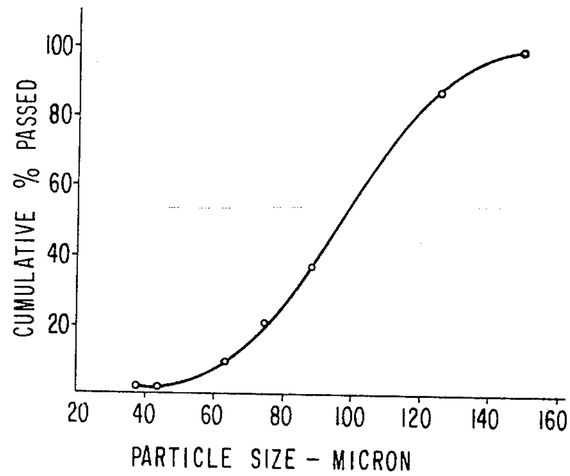


FIG. 4



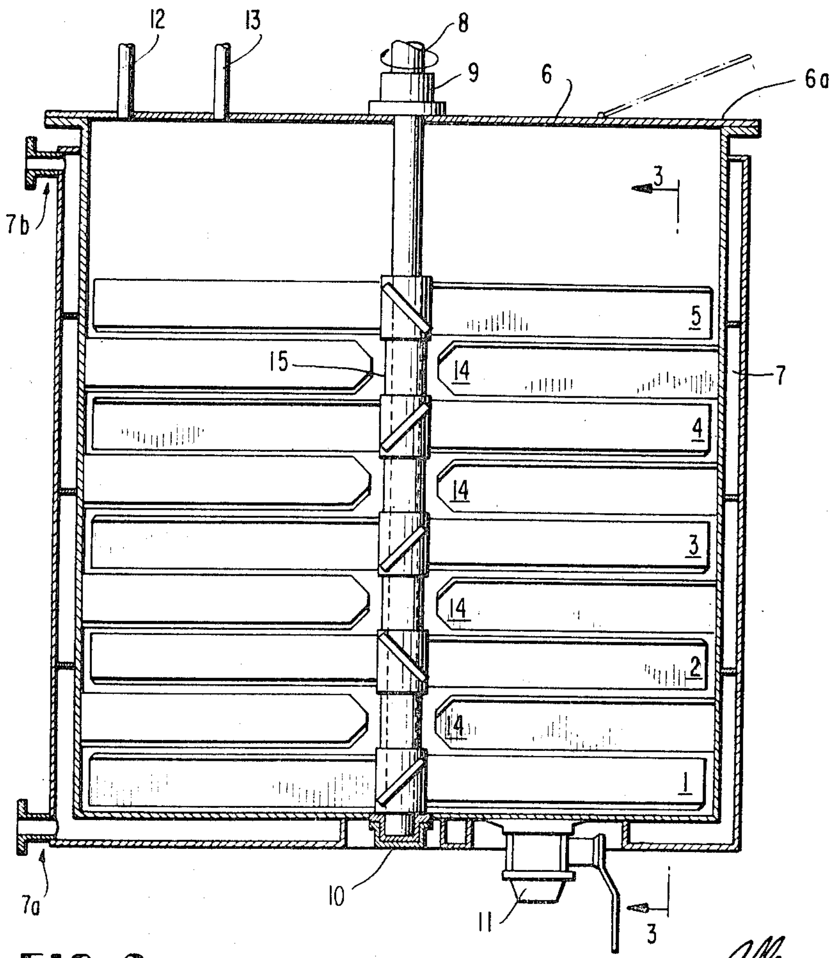


FIG. 3

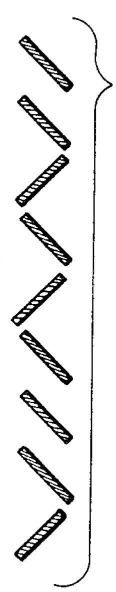


FIG. 2

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HIGH SHEAR MIXING APPARATUS FOR MAKING SILICA GELS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a novel, internally baffled and agitated high shear mixing apparatus.

2. Description of the Prior Art

The provision of apparatus which can be employed to obtain thorough and complete mixing of various ingredients or chemical reactants has been a long sought-after goal. Various solutions to the problem of obtaining thorough and uniform admixture of various materials have been proposed. Many of the proposed solutions relate to the use of some combination of baffles and rotating agitating means or blades within a confined mixing zone.

This type of mixing apparatus is illustrated by the disclosures of U.S. Pat. Nos. 634,093, 1,138,201, 1,520,375, 1,854,732 and 3,063,815. Each of these disclosures relate to the use of some combination of baffles and agitator blades in order to obtain improved mixing and illustrate the variety of different, although similar, arrangements of such means which have been brought to bear on the problem.

However, the degree of uniform, high shear mixing obtainable with apparatus presently available leaves something to be desired. Although presently available apparatus is perfectly suitable for applications which do not require extremely uniform high shear forces, the effectiveness of such apparatus has left something to be desired in the case of certain processes in which highly uniform application of the shearing forces is particularly advantageous.

One such process is the large scale production of silica gel, particularly the production of silica gel in accordance with the method set forth in copending application Ser. No. 750,734, filed on Aug. 6, 1968, now U.S. Pat. No. 3,652,215. For convenience, the apparatus of the present invention will be described and exemplified by reference to this specific process, although it will be understood that the present apparatus is particularly applicable to any mixing process in which the application of highly uniform shearing forces is desired.

In addition to the afore-mentioned application which describes a method of preparing a xerogel-type silica gel, copending applications Ser. Nos. 750,733 and 766,693, now U.S. Pat. Nos. 3,652,214 and 3,652,216, respectively also describe similar processes. Each of the three applications describe a method which comprises critically controlled steps of precipitation of a sodium silicate solution to form a hydrogel; heat-aging the hydrogel under specific temperature, time and pH limitations; reducing the sodium ion concentration of the hydrogel below a certain point; reducing the gel particle size by high shear mixing; and removing substantially all the water from the gel by a drying step.

In Ser. No. 750,734, a drying step is disclosed which comprises displacing the water from the gel by use of a suitable organic solvent (e.g., a surfactant, an alcohol, acetone, etc.) which can displace the water and reduce the surface tension of the wetting agent in the pores of the gel, followed by drying the gel.

Ser. No. 750,733, discloses a method of drying the gel which comprises a vacuum freeze-drying process to

remove essentially all the water, wherein the gel is frozen at a temperature between −100°C and −10°C and the water is then vacuum sublimed from the gel.

Lastly, in Ser. No. 766,693 there is disclosed a drying procedure which comprises adding a non-water miscible solvent which forms an azeotrope with water when distilled and distilling the azeotrope so as to remove substantially all the water under specified conditions.

In the aforesaid method for the production of silica gel, the reagents are admixed in a suitable reaction vessel and subjected to agitation in order to obtain as thorough a mixing of the reactants as possible. As it has been found that non-specific agitation tends to produce a gel which varies in particle size and other physical properties from batch to batch the reactions are usually subjected to high shear mixing before the drying of the gel in order to obtain uniformity in particle size between various lots of silica gel produced.

In the preparation of high pore volume silica gel, it has been found to be necessary to conduct the polymerization with thorough and extremely turbulent agitation This violent gitation is necessary for a variety of reasons.

Unless the agitation is thorough and extremely turbulent at the time of gelation, there is a tendency to form agglomerates of the gel which tend to separate from the bulk of the gel suspension until dissipated by the lowering of the pH of the reaction mixture. The delay in disintegration of such agglomerates causes the gel contained therein to be neutralized at a slower rate than the remainder of the gel formed, which results in the production of a product possessing non-uniform pore volumes.

After gelation, the product is heat aged while maintaining the pH within a specified narrow range. Inadequate agitation tends to cause a non-uniform pH level, resulting in a pH gradient across the gel particles. Such gradients tend to result in undesirable variations in physical properties of the final silica gel product.

In order to insure efficient leaching of alkali from the gel during the subsequent washing operations, it is necessary that the gel possess a uniform, fine particle size. Variations in particle size will result in uneven leaching of the alkali during the washing operations which, again, would result in uneven product properties. The application of uniform shearing forces throughout the reactant mixture would result in a product possessing uniform particle sizes and thus overcome this problem.

Further, the thorough and efficient agitation of the reactants and gelled products avoids the necessity of a separate homogenization step before the drying of the gel, which step has heretofore been normally required in this art in order to insure uniform particle size. The elimination of such a step results in self-evident economies.

SUMMARY OF THE INVENTION

Applicants have discovered that very high shear mixing can be obtained by the use of a particular apparatus of the agitator-baffle type, in which stationary and movable sets of blades are arranged in a specific configuration with respect to each other. The specific design of the mixing apparatus of the present invention permits the obtaining of uniform and controlled application of high shear forces which result in extremely thorough and efficient agitation of ingredients or reactants with which the apparatus may be charged.

Essentially the mixing apparatus of the present invention comprises a vertical vessel having cylindrical walls, a vertical driven shaft disposed centrally therein, a plurality of movable sets of flat blades secured to said shaft for rotation therewith, each of said movable sets being spaced equidistant from each other along the length of said shaft with the blades in each set extending radially outwardly from said shaft in equally spaced relation and pitched at an angle with respect to the axis of said shaft, a plurality of sets of stationary flat blades secured to said cylindrical wall of said vessel, each of said stationary sets being spaced equidistant from each other along the length of said shaft with the blades in each set extending radially inwardly from said wall toward said shaft in equally spaced relation and disposed at an acute angle with respect to the axis of said shaft, said stationary sets being located in alternate relation with said movable sets with substantially identical clearances therebetween and with the blades in selected sets being pitched in the opposite direction with respect to the pitched blades in other selected sets, the blades of each movable set being offset in the same circumferential direction from the blades of the adjacent movable set thereabove by equal angular increments.

DESCRIPTION OF THE DRAWINGS

FIG. 1 is a plan view of one embodiment of the apparatus of the present invention, illustrating the arrangement of the stationary and movable sets of blades therein.

FIG. 2 is a side elevation of the apparatus of FIG. 1, modified as explained below for purposes of illustration.

FIG. 3 is a sectional view taken along line A — A of FIG. 2, illustrating the pitched configuration of the various blades.

FIG. 4 is a graphic illustration of the particle size distribution of silica gels produced in the apparatus of the present invention.

The apparatus consists of a vertical, cylindrical tank with a flat top and bottom. The top lid **6** contains a partial hinged door **6***a*, which may be used for inspection and cleaning. The sides and bottom of the apparatus may be jacketed as shown at **7** and provision made for the introduction and removal of heating or cooling fluid to the jacketed portion at **7***a* and **7***b*. Insulation, for example foam or glass fiber, (not illustrated) may be applied to the exterior of this jacket.

As illustrated, the agitator consists of at least **5** rows of 4-bladed movable sets **1**, **2**, **3**, **4** and **5**, mounted on a vertical shaft **8**, each blade being pitched at an angle of 45°. However, the pitch of the blades can be varied from the disclosed 45°pitch, although a 45° pitch provides the advantage of being able to reverse the direction of agitation for another application of the apparatus; for example, when working with a suspension where the solid is lighter than the medium. A pitch greater than 45° (e.g., 60°) would result in more agitation but would require more power and would not necessarily provide more shear; while a pitch lower than 45° (e.g., 30°) would give less mixing and require more, or larger, blades to fill the tank.

Between these movable blades in the vertical direction are mounted **4** (or more) rows of horizontal stationary sets of blades **14** positioned 180° apart and also pitched at an angle of 45°. These horizontal stationary blades are mounted to the vertical walls of the vessel. As illustrated, each such stationary set contains two blades, although as will readily occur to one skilled in the art, additional blades could be employed in such sets, although additional blades would necessarily increase the power required to turn the agitator blades. In addition, the number of rows of blades is not limited so long as the apparatus remains a "vessel" instead of a "column."

The stationary paddles should not be positioned at the bottom of the vessel since this would inhibit the complete and thorough agitation required by the process for producing the silica gel product described herein.

It should be noted that agitator blade sets **1** to **5** are staggered with respect to each other, each at an angle of 18°, as shown in the plan view of FIG. **1**. In the side elevational view of FIG. **2**, however, the agitator blades are shown aligned vertically instead of being staggered. This method of illustrating the apparatus has been employed in order to more clearly illustrate the pitched configuration of the various blades, clearly shown in Section **3—3** of FIG. **2**, and should not be construed as an illustration of the actual positions of the movable sets of blades, which are, in reality, staggered as shown in FIG. **1**.

It should be noted that any arrangement of the rotating blades and stationary paddles is possible, as long as the arrangement selected provides the intimate and thorough mixing required to minimize the concentration gradients in the system equivalent to the preferred design shown above.

The agitator, comprising blade sets **1** to **5** and vertical shaft **8**, is driven by a suitable motor, preferably combined with a variable speed drive and reduction gear coupled to the vertical agitator shaft. Various combinations of motor and gears can be employed in order to obtain any desired range of speed and/or power. In the apparatus used in the following specific examples, the vessel possessed a 6-foot diameter and the agitator possessed a speed range of 5 to 50 RPM. It will be understood, however, that the vessel size and speed range can be varied at will and the present invention will not be limited by the above.

The blades of the present apparatus preferably have square edges and the horizontal edges of the blades and paddles are preferably parallel to each other and spaced as set forth below.

The ends of the agitator blades are illustrated as being square, but can be slightly rounded if desired. The shear action occurs along the front (i.e., leading) edge of the blades as they rotate and little, if any, takes place along the end of the blades as they travel through the liquid along the wall of the vessel. The configuration of the ends of the blades should be such that there is a minimum clearance between the blade ends and the vessel wall to prevent a buildup of solids in this space.

The tapered ends of the stationary paddles is desirable since the hub end of the rotating blades should not touch the ends of the paddles when the former are slipped into position along shaft **8**.

A flanged ball bearing **9** at the top of the unit supports the drive shaft and a bushing **10** stabilizes the lower end of the shaft. Spacers **15** between the rotating horizontal paddles maintain the proper spacing.

A quick opening valve **11** may be located at the bottom in order to drain the tank.

Reactants or the ingredients to be mixed may be added at inlets **12** and **13**.

Various additional instrumentation may be employed, as is well known and conventional in the art. For example, a direct and continuous reading temperature gauge and pH meter may be installed. The temperature may be automatically controlled for both cooling and heating cycles and, in addition, automatic control of the addition of reactants may also be achieved, as by control of the addition of an acid in response to the pH of the mixture.

DETAILED DESCRIPTION OF THE INVENTION

In operation, agitator blades of sets **1**, **3** and **4** are angled so that they tend to lift the ingredients in the mixer, while the blades of sets **2** and **5** are angled so that they tend to push the ingredients being mixed in a downward direction. The rotating sets of blades are keyed to the drive shaft, the keyways being successively 18° apart, which configuration assists in decreasing the magnitude of the power impulses required.

The clearance employed between the movable sets of blades and the stationary sets of blades, as well as between the ends of the rotating blades and the vertical mixer wall may vary between one-eighth inch and 2 inches, a spacing of one-half inch being preferred. The aforementioned clearances are the preferred dimensions for the production of the uniform silica gel product described herein. The spacing which is chosen is as small as is commercially practicable but sufficient to maintain suitable spacing between the various components to prevent accidental collisions due to vibration or wear of the components.

The clearance may be increased for products other than the silica gel described herein, bearing in mind that larger clearances result in less shear action and would necessitate greater rotational speed to compensate therefor.

The superior high shear mixing which may be achieved as a result of the improved reactor design of the present invention will be illustrated in the following examples by the affect upon a silica gel product prepared in accordance with the aforesaid application Ser. No. 750,734. The silica gel product obtained in accordance with the process of this application possesses a narrow pore diameter distribution primarily in the range of from 300 to 600 A., a surface area in the range of from 200 to 500 m^2/g and stability at temperatures of up to 2,000°F, even when subjected to fluidized processing.

The terminology "narrow pore diameter distribution" indicates that 70 percent, or more, of the cumulative pore volume is in the pore diameter range of 300–600A. when measured by N_2 adsorption by the B.E.T. Method. In addition, the poor volume of the xerogel-type silica gel product varies from 2.0 to 3.5 cc/gr. when measured by N_2 adsorption by the B.E.T. Method.

The properties of the silica gel obtained, particularly the porosity characteristics, are discussed in terms of pore volume (PV), surface area (SA), and average pore diameter (PD), where $PD = 4PV/SA$. Determinations of the values for the various properties are made by nitrogen absorption-desorption techniques well known in the art and described in detail in the Journal of the American Chemical Society, Volume 60, Page 309 (1938), "Journal of Catalysis," Volume 2, Page 111 (1955).

The first example describes a preferred method for carrying out the preparation of the silica gel employing the apparatus of the present invention, to obtain a silica gel with the desired physical properties and illustrates the consistency of the results obtained. The remainder of the examples illustrate trials with other types of mixers and agitators.

EXAMPLE I

2,090 pounds of sodium silicate solution containing 28.7% SiO_2 and 8.9% Na_2O were added to 387 gallons of deionized water in the reactor illustrated in FIGS. **1** and **2** and described above and cooled to 5°C with agitation of 20 RPM.

Approximately 250 gallons of 12.75 weight percent sulfuric acid were added at the following rates:

a. 40 percent of the acid was added at a constant rate over a period of 1 hour, with the agitator at 20 RPM.

b. the remainder was added over a period of 45 minutes with agitation at 28 RPM.

The final pH of the gel was adjusted to 5.0 to 5.5 and the SiO_2 content was approximately 8.5 percent.

The pore volume of the silica gel made as described in this example as well as others made in subsequent runs are listed in Table I. The reproducibility from batch to batch as a result of the specific design of the reaction of the present invention can be seen.

The consistency of the results after heat aging is also shown in the appropriate column of Table I.

TABLE I

	After Polymerization		After Heat Aging	
	Pore Volume cm^3/g	Surface Area m^2/g	Pore Volume cm^3/g	Surface Area m^2/g
1	3.12	760	2.63	337
2	2.56	775	2.77	370
3	2.67	897	2.74	363
4	2.88	558	2.74	346
5	2.72	661	2.95	376
6	2.72	473	3.01	366

In addition, the first silica gel product was coated with catalyst which reduced the PV to 2.43 and then was heated to 1,800°F with only a slight change in values:

$$PV = 2.28\ cm^3/g,\ SA = 315\ m^2/g$$

The particle size distribution curve of the material produced in Example I is shown in FIG. 4. This shows a narrow distribution of the particles between 90 and 140 microns.

EXAMPLE II

Three different types of commercially available mixers were used for preliminary silica gel polymerizations. They were studied and modified when necessary to obtain the best design for the reactor. The data obtained demonstrates the superiority of the reactor of the present invention. The amount of reagents used in each experiment were less then in Example I but were used in the same proportions and with the same technique as described in Example I so that the results, as listed in Table II, are comparable with those of Example I.

The turbine reactor consisted of a small vertical tank having an approximate capacity of 15 gallons with provisions for various types of agitator and baffle arrangements as noted in Table II. The agitator speed was varied during the experiments from 160 to 260 RPM.

The Kettle mixer was round bottomed, cylindrical 60-gallon tank similar to those used in restaurants and bakeries for food preparation. Several impeller designs were used: agitators with scraper, paddle blades, and beaters which were geared for dual rotation so that as each agitator rotated in the usual way, the set of beaters also revolved in a circular manner. This method was used to assure uniform agitation of the entire contents of the kettle. The rate of agitation was controlled throughout the experiment (i.e., the RPM varied from 68 to 160).

The shear bar reactor experiments were conducted in 18-gallon size batches. The four impeller blades were elliptically shaped and staggered so as not to pass the opposing stationary blades at the same instant. The agitator was driven at a RPM which varied from 50 to 90 throughout the experiments.

In all three of the above experiments, the agitation rate was varied to give what visually looked to be adequate agitation for each stage of the polymerization. The rate was varied within the above-defined limits during each run, and the same applies to the remaining examples.

Column 4 of Table II lists the pore volume and surface area for representative runs after gellation in the above three reactors. Variation in the results between similar runs are evident.

EXAMPLE III

This example illustrates that even when a precipitated gel which has the desired properties after gellation is obtained without using the reactor of the present invention, those properties can be destroyed during heat aging.

A further and necessary step in silica gel manufacture is heat aging of the gel after formation. At the proper pH, the slurry of silica gel in its mother liquor is aged so as to obtain the desired properties. This is achieved by raising the temperature at a predetermined rate and holding the suspension at the desired minimum temperature for the necessary length of time. This time-temperature relationship is set forth in the above-identified applications. An important part of such heat aging is the control of the pH of the suspension within a narrow range during the heating. Inadequate agitation, as indicated above, will result in a non-uniform pH level through the particle and variation in the physical properties of the finished silica gel.

Table II indicates that for runs SS-16, SS-27, SS-29, KM-1, KM-2, KM-3, BM-1 and BM-10, even when properties of the polymerized gel obtained are as desired as shown by the Example II results, these properties can be destroyed during the heat aging step, even though proper overall heat aging conditions are respected.

EXAMPLE IV

This example illustrates the effect of reactor design in the washing step of the silica gel. Subsequent to the polymerization and heat aging of the silica gel, a washing operation is carried out to remove sodium from the gel as disclosed in the afore-mentioned applications. As pointed out previously, if the silica gel particles are too large or have been allowed to agglomerate during polymerization due to inadequate agitation, then the washing operation will be ineffective for the efficient removal of the sodium ions and large amounts of sodium will remain in the interior of the gel particles even though the content of sodium in the effluent water indicates that the product has been thoroughly washed (i.e., contains less than 20 ppm of sodium).

Table II lists the physical properties of silica gels produced in each of the three experimental reactors. The presence of high concentrations of sodium is revealed by a significant lowering of the pore volume of the gel when heated to 1800°F. Test runs SS-12, SS-18 and BM-4 show that they have shrunk, whereas the gel obtained in accordance with Example I diminished much less in pore volume.

TABLE II

Reactor type	Agitator	Baffles	Example 2, after gellation		Example 3, after heat age		Example 4, after 1,800° F.	
			PV	SA	PV	SA	PV	SA
Turbine reactor:								
SS-12	4 flat blades	4 not pitched	2.52	686	2.60	313	1.62	242
SS-15	do	do	1.55	537	1.55	327		
SS-16	2 axial flow	do	2.39	542	1.75	237		
SS-18	do	do	2.74	618	2.59	299	1.42	287
SS-27	4 axial flow	1 not pitched	2.41	352	2.28	321		
SS-29	do	do	2.38	578	1.62	245		
Kettle mixer:								
KM-1	3 bar agitators with scrappers	0	2.33	613	1.77	191		
KM-2	3 perforated paddle blades	0	2.84	668	1.49	266		
KM-3	3 beater blades	0	2.06	337	1.76	304		
Bar mixer reactor:								
BM-1	2 cylindrical bars	2 straight	2.85	631	2.31	322		
BM-4	do	do	2.34	827	2.42	358	1.95	307
BM-10	do	do	2.73	388	1.85	364		

We claim:

1. High-shear mixing apparatus comprising:

a vertically disposed cylindrical vessel provided with a centrally located rotatable driven shaft having a plurality of sets of horizontally disposed and pitched flat blades extending radially outwardly from said shaft toward the interior surface of said vessel, the end of each blade being fixedly attached to said shaft and thereby rotatable with said shaft, the blades of each set of rotatable blades being positioned equidistant around said shaft;

a plurality of sets of stationary, horizontally disposed and uniformly pitched flat blades extending radially inwardly from the interior surface of said vessel toward said shaft, the end of each stationary blade being secured to said interior surface of said vessel, each set of stationary blades comprising at least two blades positioned equidistant around the interior surface of said vessel;

said sets of rotatable blades alternating with said sets of stationary blades along the length of said shaft, with the lowermost set of blades being rotatable, the clearance between each vertically adjacent set of rotatable and stationary blades and between the free ends of the rotatable blades and the interior surface of the vessel varying from one-eighth to 2 inches;

wherein the blades of each rotatable set are uniformly angularly offset in the same circumferential direction from the blades of the next vertically adjacent set of rotatable blades with the angle of offset being such that the blades of the lowermost and uppermost set of rotatable blades are offset by the same increment as the blades of the vertically adjacent sets of rotatable blades; and

wherein the blades of selected sets of rotatable blades are pitched opposite to the pitch of the blades of other selected sets of rotatable blades and to the pitch of the stationary blades.

2. The apparatus of claim **1**, wherein each of said blades is pitched at an angle of 45°.

3. The apparatus of claim **1**, wherein each of said sets of rotatable blades contains four blades.

4. The apparatus of claim **1**, which contains five rotatable sets of blades and four stationary sets of blades, each stationary set containing two blades.

5. The apparatus of claim **1** comprising, in addition, a jacket disposed around said vessel.

6. The apparatus of claim **1** wherein said angular offset is about 18°.

7. The apparatus of claim **1**, wherein said clearance is about one-half inch.

8. The apparatus of claim **4**, wherein the second and fifth rotatable sets of blades, the first set being the lowermost set in the vessel, are pitched in a direction opposite to the pitch of the other rotatable sets of blades.

9. The apparatus of claim **1** wherein at least five sets of said rotatable blades are provided and wherein at least four sets of said stationary blades are provided.

10. The apparatus of claim **1** wherein the number of sets of said stationary blades is equal to one less than the number of sets of said rotatable blades.

11. The apparatus of claim **10** wherein the uppermost set of blades is rotatable, the blades of said uppermost set being pitched downwardly, and wherein the blades of the lowermost set of rotatable blades are pitched upwardly.

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