United States Patent Office 3,154,496 Patented Oct. 27, 1964

3,154,496

PROCESS FOR PRODUCING A QUICK DISSOLVING AGGLOMERATED PERBORATE

Arnvid Sverre Roald, Cincinnati, Ohio, assignor to The Procter & Gamble Company, Cincinnati, Ohio, a corporation of Ohio

No Drawing. Filed Sept. 4, 1962, Ser. No. 221,369
3 Claims. (Cl. 252—99)

This invention relates to a process for preparing quick dissolving agglomerates of finely divided particulate perborate. Specifically, this invention relates to an efficient method for agglomerating particulate perborate by means of a spray-on of a silicate solution.

Perborate for use in the bleaching of clothes and other fabrics is normally prepared in the form of fine particles because perborate prepared in large crystals or compact agglomerates is very slow dissolving in water. Granular detergent compositions are more desirable if they contain granular perborate which will dissolve rapidly in water. In addition, it is often necessary to mix the granular perborate with detergent composition particles of a relatively large size and low bulk density. It is therefore desirable to have particles of perborate of a large size and relatively low bulk density which will dissolve rapidly in water and yet not tend to segregate from the other particles in granular detergent compositions.

Accordingly, it is an object of this invention to provide an efficient process for preparing quick-dissolving, nonsegregating agglomerates of fine particulate perborate.

It is another object of this invention to provide such a process in which the agglomeration is accomplished by means of a spray-on of a silicate solution.

It is a more specific object of this invention to provide a preferred process in which the spray-on is accomplished in a rotating drum having multiple baffles.

The objects of this invention can be accomplished by a process comprising the steps of (1) forming a mixture of finely divided particulate sodium perborate tetrahydrate and a particulate hydratable inorganic salt selected from the group consisting of disodium orthophosphate, trisodium orthophosphate, sodium carbonate, sodium pyrophosphate, the corresponding potassium salts, sodium tripolyphosphate and mixtures thereof; (2) forming said particulate mixture into a falling curtain; (3) spraying onto the particles in said curtain, as an agglomerating agent, a sodium silicate solution in a finely divided form having an average by volume diameter of from about 20 to about 150 microns, the ratio of $SiO_2:Na_2O$ in said silicate ranging from 2.6:1 to 3.8:1 and the percentage of water in said solution being from about 55% to about 70% by weight of said solution; (4) contacting with each other the particles having received said spray-on treatment in a tumbling bed; whereby the said perborate particles and said hydratable inorganic salt particles are agglomerated when the hydratable inorganic salts dehydrate said silicate solution sufficiently to form solid silicate bonds between said particles, the agglomerated particles of said perborate, hydratable inorganic salt, and silicate having an average by weight particle diameter of from about 200 to about 700 microns and having a bulk density in the range of 0.4 to 0.7 grams per cubic centimeter. The particles in said curtain should fall with a vertical velocity less than that achieved in a free fall of 10 feet (preferably less than 6 feet) starting with zero initial vertical velocity and the thickness of said tumbling bed being less than 20 inches (preferably more than 2 inches and less than 12 inches) whereby undue compaction and break-up of said agglomerates are avoided.

As used herein, an "average by weight diameter" or "average by volume diameter" refers to the diameter of a particle having the average weight or volume of the particles.

It is essential in the process of this invention to have a falling curtain of perborate and hydratable inorganic salt particles. Spraying the silicate solution onto a tumbling bed of such fine particles will not give the desired agglomerate characteristics, i.e., quick-dissolving and non-segregating. The agglomerates, having a larger particle size and a lower bulk density, tend to congregate at the top of a tumbling bed so that there is a greater tendency for further agglomeration of the already agglomerated particles than for agglomeration of the smaller particles. A falling curtain, on the other hand gives the smaller particles at least an equal chance of being contacted by the silicate solution droplets. This curtain can be prepared in a variety of ways. It is essential that the curtain be formed so as to avoid compaction and break-up of the finished agglomerates. This preferably involves forming the curtain with an initial downward component of velocity of zero and with a minimal horizontal component of velocity. It also involves having a minimum free fall of the particles. A preferred method, as will hereinafter be more fully described, is to form the curtain in a rotating drum having multiple baffles. However, any method of forming the curtain which meets the standards hereinbefore mentioned, will be suitable. Examples of other methods of curtain formation include letting the particles fall from a simple hopper or from the end of a conveyor belt.

The tumbling bed is essential in the present process to bring those particles to which the silicate solution droplets have adhered into intimate contact with other particles to form agglomerates. In a rotating, baffled drum this tumbling bed is formed by having sufficient particulate material present, in excess of that required to form the falling curtain, to maintain, in the lower part of the drum, the desired bed height. When the falling curtain is formed by a means other than a rotating baffled drum, the tumbling bed can be formed, for example, in a rotating substantially horizontal drum into which the particulate curtain is directed.

The perborate of this invention is in the form of finely divided particulate matter having an average by weight diameter of from about 30 to 300 microns, preferably 50 to 200 microns. The perborate with the above average particle size range preferably has a particle size distribution in which from 0 to 20% is on 35 mesh, from 0 to 50% is on 48 mesh, from 0 to 63% is on 65 mesh, from 0 to 87% is on 100 mesh, and from 10 to 96% is on 200 mesh. All mesh figures herein refer to Tyler Standard Screen sizes. The perborate is present in the finished agglomerate in an amount from about 40% to about 90% by weight (preferably 55% to 70%). This particulate perborate can have many physical forms. The particles can be in the form of flat plates, approximate spheres, etc. The rate of solubility and the ease of formation of agglomerates will be in part dependent upon the physical form but the invention is equally operable with any of the above physical forms. Particle sizes of perborate smaller than those hereinbefore mentioned will require more silicate solution for agglomeration and consequently, more hydratable inorganic salts to take up the water from the silicate for the same size of agglomerate so that the resulting agglomerate will be poorer in floc grade (this floc is a slowly soluble silicate which is objectionable in the laundry water). Particle sizes of perborate coarser than those hereinbefore mentioned, result in a slower overall solubility rate for agglomerates of the same size as those made with the specified particle sizes.

The hydratable inorganic salt hereinbefore mentioned should have an average by weight diameter of from about 20 to about 400 microns, preferably from 100 to 300 microns. Said salt with the above average particle size range preferably has a particle size distribution in which from 0 to 1% is on 20 mesh, from 0 to 35% is on 35 mesh, from 0 to 95% is on 65 mesh, from 1 to 99% is on 100 mesh, from 11 to 100% is on 200 mesh, from 15 to 100% is on 270 mesh. As in the particulate perborate, the nature of the crystal also affects the behavior of the hydratable inorganic salt. Hydratable inorganic salts having a light density such as those prepared by a spray-drying process are preferred. It is also desirable that the average particle size of the phosphate and the perborate be similar. If one component is very much coarser than the other, the resultant agglomerate may not be of uniform composition and more silicate will be needed to form uniform agglomerates of the desired particle size. Since a function of the hydratable inorganic salt is dehydration of the silicate solution to form a solid bond which holds the agglomerate together, there should be from 5% to 40%, preferably 10% to 30%, by weight of the hydratable inorganic salt on an anhydrous basis in the final agglomerates. The amount should be selected within these ranges so as to take up, as water of hydration, a sufficient amount of the water from the silicate solution to form solid interparticulate bonds so that agglomerates are formed. Preferably, the inorganic hydratable salt will be at least 60% hydrated in the finished agglomerate. This amount will vary with the amount of silicate solution sprayed on, the $SiO_2:Na_2O$ ratio, and the amount of water in the silicate solution. The silicate in the agglomerating solution should have a ratio of $SiO_2:Na_2O$ ranging from 2.6:1 to 3.8:1. The preferred ratio is 3.2:1. At ratios lower than 2.6:1, an equal weight of silicate gives poorer agglomeration. At ratios higher than 3.8:1 more floc is formed. Said silicate solution should be sprayed on in an amount from about 5% to about 40%, preferably 10% to 30% of the final agglomerated product, and said silicate solution should contain from 55% to 70% water. This corresponds to a percent by weight of silicate solids in the final agglomerate of from 1.5% to 18%, preferably from 3.0% to 13.5%. This silicate solution is sprayed onto the falling curtain in a finely divided form having an average by volume diameter of from 20 to 150 microns. The size of the droplets should always be of the same magnitude or smaller than the size of the particles of hydratable inorganic salt and/or perborate. The amount of water in the silicate solution depends upon the $SiO_2:Na_2O$ ratio and the viscosity needed to form finely divided droplets. The optimum amount of silicate solution sprayed onto the perborate-hydratable salt mixture will vary with the size of the particles in the perborate-hydratable salt mixture, the concentration of the silicate solution, the $SiO_2:Na_2O$ ratio, and the desired size of the agglomerates. The silicate solution should be dehydrated to a water content of less than about 55% by weight of the silicate-water mixture in the final agglomerate.

Minor amounts of inert ingredients and additives such as other inorganic salts, dyes, etc., can be included, if desired, in the agglomerate either by initial incorporation in the perborate-hydratable salt mixture or in the silicate agglomeration solution.

As hereinbefore mentioned, the preferred equipment for forming the falling curtain of the perborate-hydratable salt mixture is a rotating drum having multiple baffles.

Such a drum normally has a length of from about 2 ft. to about 12 ft., preferably from about 4 ft. to about 8 ft.; a diameter of from about 2½ ft. to about 10 ft., preferably from about 3 ft. to about 6 ft.; and has a circumferential distance between baffles of from about 2 in. to about 20 in. The baffles preferably have a baffle depth (width) of from about 1 in. to about 8 in., depending on the diameter of the drum, and a slope from the radius of from 5° above the radius to 25° below the radius, preferably from 5° to 15° below the radius, said slopes being measured on the side of the drum where the curtains are formed. The drum turns at a speed of from

about 3 to about 30 r.p.m., depending upon the diameter of the drum.

The selection of the exact dimensions for optimum practice of the process is dependent upon several factors. For example, smaller baffles are preferred in drums with smaller diameters. If too much material is carried up and discharged during drum operation into a falling curtain, a smaller percentage of material in the curtains is hit by the silicate agglomerating spray and the undesirable compacting and breaking of the agglomerates is increased relative to the agglomerating action. However, the baffles should not be too small, since then they will not lift a sufficient amount of material to discharge suitable falling curtains.

The size, spacing and slope of the baffles will also be related to the speed of rotation of the drum. For instance, the slope of the baffles can be adjusted to determine when the particulate material held on the baffle discharges into a falling curtain. Similarly the speed of rotation of the drum will help determine when the particulate material discharges and will affect the number and slope of the baffles required. The faster the speed, the more times a baffle will discharge in any given time period and the fewer baffles will be required to maintain continuous falling curtains in front of the silicate agglomerating spray. If there are too few baffles there will not, at all times, be falling curtains in front of the agglomerating spray; but on the other hand, too many bafflles give no additional advantage.

The speed of the drum, as hereinbefore mentioned, will affect the time when the baffles discharge their particulate charge into a falling curtain. If the speed is too slow, the baffles discharge too soon. If the speed is too fast, the particles are thrown toward the opposite side of the drum.

The drum is normally sloped. The degree of slope is chosen to give the optimum retention time of particulate and agglomerated material at the desired through-put. If too much material is retained in the drum, the individual particles and agglomerates are subjected to excessive dropping, tumbling and bed thickness which tend to compact them and to some extent to break down the agglomerates. If there is too little material in the drum, the thickness of the falling curtain will be inadequate to trap the agglomerating spray from the spray nozzles. Droplets of agglomerating liquid will then hit the drum or its baffles and cause excessive build-up and generally poor operation. The precise optimum slope must be determined more or less empirically for each installation. The drum should contain at least one atomizing device capable of forming finely divided droplets of the silicate solution wherein the droplets have an average by volume particle diameter of from 20 to 150 microns. Of course, the atomizing device will have to be capable of forming droplets of the same magnitude or smaller than the size of the particles of hydratable inorganic salt and/or perborate. Any type of atomizing device which produces droplets having this particle size is acceptable. An example of such a device is a two-fluid nozzle, in which the atomizing fluid for the silicate solution is compressed air at a pressure of from 20 to 100 p.s.i.g. The atomizing device or devices should preferably be positioned so as to afford maximum contact between the silicate droplets and the particles in the falling curtain. This will normally be accomplished by directing the spray onto the face of the falling curtain.

Other solids-liquids contacting devices can be used to form the equivalents of a falling curtain and a tumbling bed of this invention. The critical features required are that the smaller particles as well as the coarser particles be exposed at least equally to the silicate agglomerating spray, that the particles which have been contacted with the silicate be brought into contact with other particles, and that excessive compacting action during and after agglomeration be avoided.

The finished perborate agglomerates prepared by the process of this invention are quickly soluble, low density particles having excellent oxygen stability. Due to the low bulk density, large size of the agglomerates, and size distribution of said agglomerates, it is possible to prepare mixtures of said agglomerates with light density granular detergent compositions which will have little tendency to segregate. The segregation tendencies are a function of the particle sizes and densities of the agglomerates and the detergent particles. For instance, if detergent particles of very low densities are used, perborate agglomerates of a relatively coarser particle size will be required to achieve optimum non-segregation qualities.

The following examples illustrate the practice of this invention.

As used herein, "density" refers to "bulk density." Also, as used herein, "improved segregation characteristics" refers to the fact that the perborate agglomerates of this invention have a reduced tendency to separate from light density granular detergents.

Example I

A mixture of 7.5 lbs. of sodium perborate tetrahydrate and 2.1 lbs. of anhydrous sodium tripolyphosphate (STP) with the densities, particle sizes, and particle size distributions hereinafter given were agglomerated in a cement mixer of about 2.5 cubic feet volume. The mixer, which had only one speed, turned at about 28 r.p.m. and had three baffles equally spaced. This apparatus in operation with its particulate charge gave a falling curtain of about one foot in height and a tumbling bed depth of about four inches.

Sodium silicate solution in the amount of 3.2 lbs. with a 3.2:1 SiO_2:Na_2O ratio and a water content of 62.5% was sprayed at a rate of 150 cc./minute onto the falling curtain using a single two-fluid nozzle. Air at a pressure of 50 pounds per square inch was used as the atomizing fluid, giving an average by volume droplet diameter of about 50μ. An agglomerate of coarse particle size and light density was obtained.

	Perborate	STP	Agglomerate
Density (gm./cc.)	0.98	1.05	0.57
Approximate average by weight particle size (μ)	70	50	310
Particle Size Distribution (Tyler Standard Screen, Cumulative percent by weight):			
On 20 mesh			1.8
On 65 mesh			84.1
On 100 mesh	1	1	
On 200 mesh	70	10	
On 270 mesh		30	
PAN	30	70	15.9

The agglomerated product has improved segregation characteristics when mixed with light density synthetic detergent granules, compared to regular crystalline perborate, and has markedly quicker solubility than unagglomerated perborate of the same particle size, providing rapid and effective oxygen bleaching action for soiled and stained clothing and other fabrics.

When stored for four weeks in closed containers at 120° F. the oxygen stability of the perborate was also improved by agglomeration.

	Percent O_2 loss		
	1 week	2 weeks	4 weeks
Crystalline perborate	13.0	53.0	63.0
Agglomerated perborate	2.5	2.5	2.5

In Example I, the particulate sodium tripolyphosphate can be replaced with particulate sodium carbonate or trisodium orthophosphate having similar characteristics with substantially equal results.

Example II

A mixture of 10 lbs. of sodium perborate tetrahydrate and 3.2 lbs. of anhydrous sodium tripolyphosphate having the densities, particle sizes, and particle size distributions hereinafter given were agglomerated in the cement mixer of Example I. This gave a tumbling bed depth of about five inches. The silicate solution of Example I was sprayed onto the falling curtain (having a height of about one foot) at the rate of 350 cc./minute until 2.2 lbs. of solution had been sprayed. Air at a pressure of 50 pounds per square inch was used giving an average by volume silicate solution droplet diameter of about 75μ.

	Perborate	STP	Agglomerate
Density (gm./cc.)	0.86	0.55	0.57
Approximate average by weight particle size (μ)	200	170	370
Particle size distribution (Tyler Standard Screen, Cumulative percent by weight):			
On 20 Mesh		4.1	6.4
On 35 Mesh	8.7	15.7	53.8
On 48 Mesh	24.8		79.4
On 65 Mesh	51.8	47.7	93.0
On 100 Mesh	80.2	65.0	
On 200 Mesh		86.6	
PAN	19.8	13.4	7.0

The agglomerate has improved segregation characteristics compared to regular crystalline perborate, and has quicker solubility when used to provide a bleaching solution than unagglomerated perborate of the same particle size.

Example III

A mixture of sodium perborate tetrahydrate and anhydrous sodium tripolyphosphate in the ratio of 10.0 to 3.2 was continuously agglomerated in a rotating cylindrical drum at a rate of 2,000 lbs./hour finished product by spraying the sodium silicate solution of Example I onto the falling curtain of the mixture formed in the drum until the finished agglomerate contained 19.1% silicate solution. The drum was six feet long and three feet in diameter, and had nine equally spaced baffles mounted on the inner periphery of the drum and extending the length of the drum, each baffle being 3¾ inches deep and sloped 10° below the radius. The drum was sloped about ½° and rotated at about 9 r.p.m. An average silicate droplet diameter of about 75μ was obtained by using five two-fluid nozzles with air at a pressure of about 65 pounds per square inch as the second fluid.

The perborate, phosphate, and agglomerates had the following analysis.

	Perborate	STP	Agglomerate
Density (gm./cc.)	0.98	0.57	0.53
Approximate average by weight particle size (μ)	70	260	390
Particle size distribution (Tyler Standard Screen) (Cumulative Percent by weight):			
On 20 mesh			9.2
On 35 mesh		25.3	60.5
On 48 mesh			81.1
On 65 mesh		95.9	89.8
On 100 mesh	1		
On 200 mesh	70		
PAN	30	4.1	10.2

The agglomerate of Example III has improved segregation characteristics compared to regular crystalline perborate, and has quicker solubility than unagglomerated perborate of the same particle size, providing effective oxygen bleaching solutions.

What is claimed is:

1. A process for producing a quick-dissolving agglomerated perborate by

(*a*) forming a mixture of finely divided particulate sodium perborate tetrahydrate and a hydratable inorganic salt selected from the group consisting of sodium pyrophosphate, sodium carbonate, trisodium orthophosphate, and disodium orthophosphate, and sodium tripolyphosphate;

(b) forming said particulate mixture into a falling curtain;

(c) spraying onto the particles in said curtain, as an agglomerating agent, a sodium silicate solution in a finely divided form having an average by volume droplet diameter of from about 20 to about 150 microns, the ratio of $SiO_2:Na_2O$ in said silicate ranging from 2.6:1 to 3.8:1 and the percentage of water in said solution being from about 55% to about 70%;

(d) contacting the particles, having received said spray-on, with each other in a tumbling bed; whereby the said perborate particles and said hydratable inorganic salt particles are agglomerated, the hydratable inorganic salts dehydrating said silicate solution sufficiently to form solid silicate bonds between said particles; the agglomerated particles of said perborate, hydratable salt and silicate having an average by weight diameter of from about 200 to about 700 microns and having a bulk density in the range of 0.4 to 0.7 gram per cubic centimeter; the particles in said curtain falling with a vertical velocity less than that achieved in a free fall of 10 feet starting with zero initial vertical velocity and the thickness of said tumbling bed being less than 20 inches, whereby undue compaction and break-up of said agglomerates are avoided.

2. The process of claim 1 wherein the perborate tetrahydrate has an average by weight particle diameter of from about 30 to 300 microns and is present in an amount sufficient to make up from about 40% to 90% by weight

of the finished agglomerate; the hydratable inorganic salt is sodium tripolyphosphate and has an average by weight particle diameter of from about 20 to about 400 microns and is present in an amount from about 5% to about 40% by weight of the finished agglomerate on an anhydrous basis; and the silicate solution is sprayed on in an amount from about 5% to about 40% by weight of the final product.

3. The process of claim 1 wherein the perborate tetrahydrate has an average by weight particle diameter of from about 50 to about 200 microns and is present in an amount sufficient to make up from about 40% to about 90% by weight of the finished agglomerate; the hydratable inorganic salt is sodium tripolyphosphate and there is from 10% to 30% by weight of the finished agglomerate of the hydratable inorganic salt on an anhydrous basis having an initial average by weight particle diameter of from about 100 to about 300 microns; sufficient silicate solution is sprayed onto the particulate mixture to make up from 10% to 30% by weight of the finished particle; the falling curtain has a downward velocity equal to or less than the velocity achieved in a free fall of six feet starting with zero initial downward velocity; and the height of the tumbling bed is less than about 12 inches.

References Cited in the file of this patent

UNITED STATES PATENTS

2,863,835	Goldsmith et al.	Dec. 9, 1958
2,972,584	Schmidt et al.	Feb. 21, 1961
2,975,142	Schmidt et al.	Mar. 14, 1961

FOREIGN PATENTS

556,437	Canada	Apr. 22, 1958