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3,086,851

BURNER FOR PRODUCTION OF FINELY DIVIDED OXIDES

Original Filed Oct. 10, 1957

2 Sheets-Sheet 1

Fig. 1

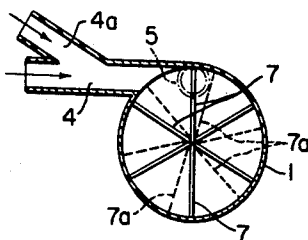
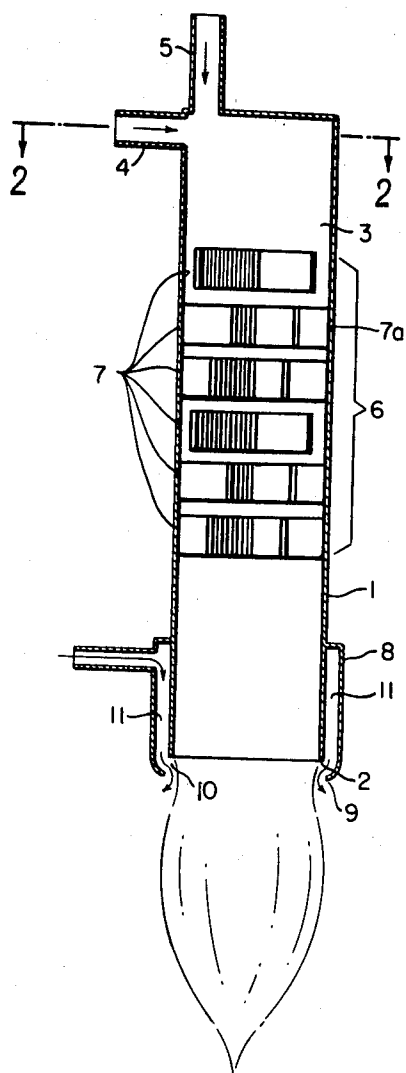


Fig. 2

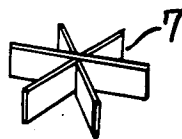


Fig. 3

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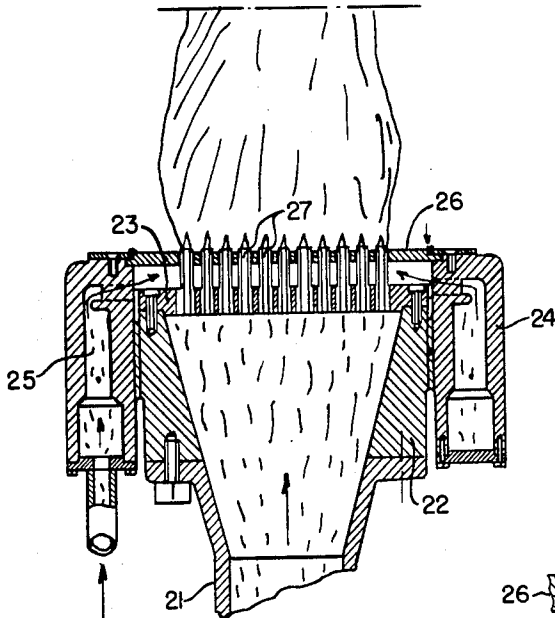


Fig. 4

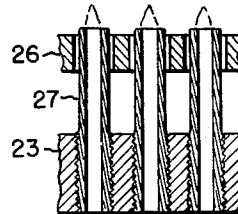


Fig. 6

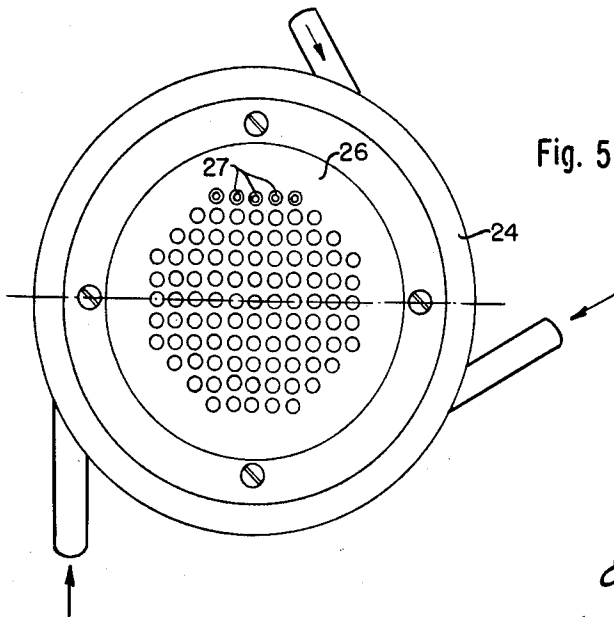


Fig. 5

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3,086,851

**BURNER FOR PRODUCTION OF FINELY
DIVIDED OXIDES**

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Original application Oct. 10, 1957, Ser. No. 689,427, now Patent No. 3,006,738, dated Oct. 31, 1961. Divided and this application Jan. 5, 1961, Ser. No. 93,006

1 Claim. (Cl. 23-277)

The invention relates to the preparation of finely divided oxides of metals and metalloids by hydrolytic decomposition in a flame of hydrolyzable volatile compounds, for example halogen compounds.

The preparation of finely divided oxides, for example silicon dioxide, by combustion of the corresponding halides, has previously been proposed. In practicing such processes, the reaction has been carried on in a plurality of small flames and the silicon dioxide deposited on cooled surfaces in motion. This procedure, for large-scale production, requires comparatively extensive engineering and financial expenditure.

It has now been found that the preparation of finely divided oxides in a flame can be substantially simplified and rendered more economical by carrying on the conversion of the volatile compounds by hydrolysis in such a manner that the gases forming water upon combustion, for example hydrogen or methane and oxygen, are first homogeneously mixed with the volatile compound to be hydrolyzed and then caused to react together in one flame. In the process according to the invention, it is not necessary to use a large number of small flames. Instead, contrary to expectation, perfectly uniform and extremely finely divided products are obtained when combustion is carried on in comparatively large flames.

This novel procedure has been by no means obvious. In similar processes it has heretofore been the practice for the reactions to proceed concurrently with a combustion, e.g. with formation of solid decomposition products within a preferential flame zone. This is true particularly in cases where the reaction concurrent with the combustion withdraws heat from the flame.

In order to overcome this disadvantage in heretofore known processes, the volatile compound to be decomposed has been blown into an already existing flame, or the initiation and maintenance of the decomposition reaction have been assisted or effected by means of special auxiliary flames. In practicing the known process described above, silicon halide has been mixed with the combustible gases, but only with a portion of the oxygen required for the reaction. As a result of this, combustion and hydrolysis has taken place chiefly in the surface zones of the many small flames, where atmospheric oxygen is freely available.

It might have been anticipated that the conduct of an endothermic reaction throughout the volume of the flame would unfavorably affect the process of combustion and the concurrent decomposition. Instead, it has been found that when homogeneous mixtures are used, the decomposition of the volatile metals or metalloid compounds and the formation of the corresponding oxides proceed uniformly and smoothly in nearly quantitative yield. It has been found especially advantageous to use initial mixtures having an oxygen content, referred to formation of water, in at least stoichiometric proportion to the content of hydrogen or hydrogen-supplying gas. In contradistinction to the conventional procedure, a flame is used which is self-sufficient with respect to the surroundings requiring no external supply of oxygen. Even when a stoichiometric mixture, associated with maximum heat concentration in the flame, is used, it is

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possible, contrary to expectation, to prevent any undesired coarsening of particles in the relatively large flames used according to the process.

Very finely divided products are obtained, if, according to one manner of carrying out the process, the compound to be hydrolyzed occurs in the gaseous mixture in as high a dilution as feasible. Thus, according to the invention, by altering the content of the gaseous mixture to be burned, the particle size of the oxides formed can be controlled by simple means. The use of this expedient leads to a concurrent change in the output of metal oxide. However, even at constant output, a more finely divided product can be obtained by supplying the oxygen or oxygen-bearing component, for example air, in the gaseous mixture, to the flame in a hyperstoichiometric proportion with respect to formation of water. Use of stoichiometric or hyperstoichiometric oxygen content, in contradistinction to previously known processes, affords optimum utilization of the hydrogen or hydrogen-supplying component used. In this way, the consumption of hydrogen can be reduced to such an extent as only slightly to exceed, for example by 10%, the amount theoretically required.

For the preparation of extraordinarily active products in which completion of the surface in the sense of elimination of lattice distortions and active centers of primary particles is prevented as far as possible, it has been found advantageous to keep the temperature of the flame as low as possible, using flame temperatures between 900 and 1200° C., especially favorable results being obtained when the flame temperature is between 1000 and 1100° C. A low flame temperature may be maintained, according to the invention, by various means. The content of the gaseous mixture in the compound to be hydrolyzed may be raised, thereby withdrawing larger quantities of heat from the flame by the decomposition of this compound. This is done at the cost of an increased particle size. On the other hand, reduction of flame temperature may also be effected, as described above, by supplying the flame with oxygen in hyperstoichiometric amounts with respect to water formation, or with inert gases as diluents, for example nitrogen. The use of the last-mentioned expedient at the same time implies a reduction in the content of the mixture with respect to the compound to be decomposed, and hence a reduction in the particle size of the oxide formed. The control means afforded by the application of these various expedients render the process according to the invention exceedingly flexible in practice, and are of substantial advantage particularly with respect to the controllable selection of a variety of products.

Reduction of flame temperature as a means of protecting solid products in order to preserve the active surface of primary particles is subject to the limitation that if the flame is too cool, its continuity is jeopardized. According to the invention, therefore, the process may alternatively be so conducted that the decomposition may take place in a hot flame, while the exposure time of the products is rendered extremely small. For this reason, according to a particular form of embodiment of the invention, short flames of great volume and small height are used. Such flames, if circular in shape, may for example be characterized by a ratio of height to diameter of 2:1 or 1:1 and below. In order to produce such flames it is proposed to make use of a rosette burner in which a plurality of small flames may unite into one large and comparatively short flame.

Since, according to a preferred form of the invention, the flame is self-sufficient with respect to oxygen, i.e. is supplied with oxygen in at least stoichiometric amounts, the process according to the invention does not require the uncontrolled supply of oxygen from the atmosphere to

the flame front, unlike known processes, in order to sustain the flame and carry on the decomposition reaction. It is consequently possible to carry on the reaction in an enclosed space, thus avoiding further dilution of the oxide formed, as well as of the other reaction products, through the uncontrolled entry of air. Therefore the oxide, as well as the hydrogen chloride formed by the hydrolysis, is obtained in maximum concentration, so that the recovery of these products is greatly simplified and can be accomplished with a minimum of equipment.

In view of the substantially uniform and homogeneous distribution of the various reagents throughout practically the entire volume of the flame, according to the invention, the penetration of air or oxygen-bearing gas over and above the amounts supplied in the mixture is in fact undesirable, since this may readily produce disturbances of the homogeneity of the flame, as turbulence, vortexes or the like. It is therefore advantageous to provide for laminar flow of the original gaseous or vaporous mixture on the way to the flame and within the latter.

As a general rule, supply of hydrogen or hydrogen-bearing gas to the flame together with the compound to be decomposed and the oxygen or oxygen-bearing gas has heretofore been avoided because the resulting sudden reaction at the mouth of the burner may readily produce oxide deposits which ultimately clog the burner orifices and interfere with the sensitive control of the process, especially in continuous operation. It has been proposed that this disadvantage be avoided by keeping the exit speed of the gas high enough so that the flame will not exist except at some distance from the mouth of the burner.

An essential factor in the successful practicing of the process is the use of suitably designed burners, of a construction such as to lend themselves to the basic features of the invention. It is especially important that the mixture of the compound to be decomposed and the gases forming the water be intimate and homogeneous, and also that it be supplied to the flame in a uniform, smooth and preferably laminar current. For practicing the process according to the invention, the most suitable burners are those which, in addition to a mixer chamber for the gases taking part in the reaction, are provided with devices in which the flow of gas can be directed and equalized. Also, the burners should be provided with means by which the mouth of the burner is reliably kept free from deposits, "streamers" etc. Subject to these restrictions, numerous different burner designs that may be used for practicing the process are conceivable.

A tube burner which has proved eminently suited to the process according to the invention is schematically shown in the accompanying drawings in which:

FIG. 1 is a view showing the burner tube and its connections in longitudinal section and the enclosing baffles in elevation,

FIG. 2 is a view in cross-section on the line 2—2 of FIG. 1,

FIG. 3 is a view in perspective of a single baffle,

FIG. 4 is a sectional view of a rosette type of burner,

FIG. 5 is a corresponding plan view, and

FIG. 6 is a fragmentary sectional view of FIG. 4 on an enlarged scale.

In FIG. 1, 1 is the burner tube proper, while the mouth of the burner is at 2. At the inlet end of the tube away from the flame, we have the mixer chamber 3 with inlets 4 and 5 for the reagents. In order to secure homogeneous mixture of the components in the mixer chamber 3, the entering gases or vapors are vigorously agitated by tangential entry of at least one of the components into the mixer chamber, while the other enters at an angle. The tangential inlet is at 4 and the axial inlet is eccentrically located at 5. Between the mixer chamber and the flame, a considerable portion of the tube is occupied by baffles 7, forming a flow-rectifying chamber 6. An arrangement of these baffles 7 is shown by way of example in the sectional view 2, in which the same reference numbers have been

used. However, the gas inlet 4 is here further sub-divided, having a branch 4a. The baffles in this case comprise flat sheets or strips of rectangular contour arranged symmetrically in radial or star-shaped formation as shown in FIG. 3 and uniformly spaced from each other with respect to the longitudinal axis of the tube. The flat plates of the baffles are disposed with their width extending parallel to the axis of the burner tube, or in the direction of gas flow. Each of the baffles 7 is radially shifted around the longitudinal axis of the burner relative to the one above it, as indicated in FIG. 2 by the dotted line 7a. The radial sheets of each baffle converge toward and intersect in the axis of the tube.

The burner functions in the following manner.

The hydrogen or hydrogen-supplying gas is introduced into the mixer chamber at the inlet 5, while the combustion air or an oxygen-supplying gas enters at the inlet 4, and the compound to be decomposed, with a conveyor gas, preferably air, is introduced at 4a. The tangential flow of the gases entering at 4 thoroughly mingles and homogeneously mixes with the hydrogen-supplying component entering perpendicularly at 5. The resulting highly agitated body of gas now flows in a divided and gradually rectifying path through the passage defined by the baffles, by which it is sub-divided into segments which, owing to the radial displacement of the baffles, are transformed into uniform non-turbulent and preferably laminar flow towards the mouth of the burner, emerging in homogeneous distribution.

According to a preferred form of embodiment of the device described, the part of the tube 1 towards the mouth of the burner is covered with a jacket 8 constricted at its extremity 9 so as to form an annular slit 10 in combination with the mouth of the burner. The jacket 9 and the wall 1 of the tube now form an annular space 11 through which a gas such as air may be introduced, so as to emerge annularly through the slit 10 and flow uniformly over the edge of the burner. This serves not only to keep the reaction away from the mouth of the burner, thus mechanically impeding the formation of solid reaction products at the mouth, but also, by increased dilution with inert gas, depresses the rate of ignition of the mixture to such an extent that the reaction fails to occur in that area. This combined physical and mechanical feature has proved highly advantageous for ensuring trouble-free operation of the burner, and the comparatively small amounts of air or other gas locally introduced do not adversely affect the homogeneity and stability of the flame to any appreciable extent.

The apparatus according to the invention offers the possibility, with a minimum of equipment, of handling large quantities in the manufacture of finely divided oxides of metals or metalloids in yields of 98% or over, referred to the compound containing the metal or metalloid. These excellent results are obtained with maximum economy of hydrogen or hydrogen-supplying gas, with resulting surprisingly low total consumption of this gas. It has been found especially desirable to control the size and surface activity of the oxide particles produced in the many possible ways, making possible an optimum adaptation of the properties of the product to the specific purpose intended at the time.

Finely divided active oxides prepared by the process according to the invention have been found especially satisfactory as fillers for natural and synthetic rubber, plastics and other molding compounds, as thickeners for liquids, as sedimentation inhibitors, as catalyst vehicles, as adsorption agents, and as thickeners, bases or active vehicles for ointments, creams, powders and other cosmetic and pharmaceutical products.

Example I

A mixture of about 20 cbm. (cubic meters) of hydrogen and of about 150 cbm. of air is passed into a burner of the aforementioned type with an orifice of a diameter

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of 40 mm. In addition to this mixture 48 kgs. of a silicon tetrachloride vapors are further introduced into the burner. That means a charge of 635 grs. of SiCl_4 per cbm. of the air-hydrogen gas mixture. A yield of 16.6 kgs. SiO_2 per hour was obtained. The bulk weight was about 25 grs. per liter and the average particle size about 10-30 mm.

The rosette type of nozzle referred to above and well adapted to produce the desired short flame of great volume is shown in FIGS. 4 and 5. It comprises a substantially circular group or nest of individual burners from which the individual jets merge in a single short flame of the full diameter of the nozzle. The nozzle is secured to the discharge end of the cylindrical burner tube 21 which may correspond to the tube 1 of FIGS. 1 and 2. It includes an annular casting 22 forming a frusto-conical chamber diverging outwardly. The larger end of this chamber is closed by a perforated plate 23. An outer concentric annular casting 24 having air passages 25 surrounds the casting 22 and is secured permanently thereto. This outer casting 24 extends outwardly beyond the plate 23 and to its outer end is permanently secured an outer circular burner plate 26. Between the plates 23 and 26 is formed a circular air chamber to which air is delivered through the passages 25. Elongated burner pipe sections or nipples 27 are secured at their lower ends in the plate 23 and are spaced from the plate 26 by longitudinal fins which provide concentric air openings about them. These nipples extend inwardly into the perforations of the plate 23 and terminate substantially flush with its inner face.

In operation the gaseous components of the process, viz., the hydrogen-supplying gas, the oxygen-supplying gas and the conveyor gas with its halide component, are supplied to the mixing chamber at the remote inlet end of the tube and passed upwardly through the rectifying chamber of the burner tube to the nozzle of FIGS. 4 and 5. By the time the gaseous constituents arrive at the nozzle they have been reduced from turbulence to a uni-

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form non-turbulent or laminar flow. The velocity of gaseous flow is reduced by passage through the expanding conical chamber of the inner casting 22. The combustible mixture then issues from the nipples 27 of the burner gently and without turbulence forming a single thick non-turbulent flame in which the hydrolyzation occurs in the gaseous mixture under conditions of high dilution. Meanwhile air or other inert gas issues as a sheath about the discharge end of the burner nipples 27 thus substantially eliminating the formation of objectionable oxide deposits which might otherwise clog the burner orifices.

This application is a continuation-in-part of my prior application Serial No. 344,840 filed March 26, 1953, abandoned in favor of a continuing application Serial No. 766,274, now U.S. Patent No. 2,990,249 of June 27, 1961, and a division of Serial No. 689,427 filed October 10, 1957, now U.S. Patent No. 3,006,738 of Oct. 31, 1961.

Having thus disclosed my invention and described in detail preferred embodiments thereof, I claim as new and desire to secure by Letters Patent:

A burner for the production of finely divided oxides of metals and metalloids by hydrolysis of volatile components, comprising a nozzle including in its structure an inner annular casting forming an outwardly diverging frusto-conical chamber, an end plate closing the larger end of said chamber and having a plurality of nipples projecting outwardly therefrom, an outer annular casting concentrically surrounding the inner casting and having an outer burner plate spaced from the said end plate, forming an air chamber therewith and being perforated to provide air passages about said nipples.

References Cited in the file of this patent

UNITED STATES PATENTS

1,536,176	Aldrich	May 5, 1925
1,874,488	Franklin	Aug. 30, 1932
2,569,699	Stalego	Oct. 2, 1951
2,630,461	Sachsse et al.	Mar. 3, 1953