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(54) METHOD OF PREPARING FINELY-DIVIDED SOLIDS

(71) We, NATIONAL RESEARCH DEVELOPMENT CORPORATION, a British Corporation, established by Statute, of Kingsgate House, 66-74 Victoria Street, London, S.W.1, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

10 This invention relates to the production of substances, including the so-called refractory materials, in a state of controlled sub-division, and is especially concerned with the production of finely divided materials with controlled surface characteristics. Refractory compounds are here considered as inorganic compounds of relatively high melting point.

Finely divided substances exhibit useful physical properties which may be exploited in a variety of applications. For example, particulate inorganic oxides are extensively used as pigments, extenders, thickening agents and filler materials for polymers and in coating compositions. For such applications, it is important to provide materials having the appropriate particle size, shape and surface character, the property of fine particle size being especially important. For many applications particle sizes of less than 5000Å are desirable and in some cases a particle size of less than 2000Å is preferred.

It has now been found that the control of particle size of inorganic oxides, carbides, nitrides and other compounds, in-

cluding the so-called refractory compounds, may be achieved.

According to the present invention, a process for the production of a finely divided solid comprises producing a non-volatile inorganic oxide in the vapour phase by heating a melt containing said oxide or a precursor thereof as hereinbefore defined with a gas stream of high temperature and enthalpy, said melt being centrifugally distributed on the inner surface of a hollow rotating body, and subsequently condensing in finely divided form the oxide or a species derived therefrom by physical or chemical modification thereof.

According to this invention, the oxide is produced in the vapour phase by impingement on the melt of a gas stream of high enthalpy, followed, if required, by chemical reaction in the vapour phase to convert the vaporized material into the desired chemical form. The vapour species formed by either direct evaporation or by subsequent chemical reaction are then condensed in a rapid but controlled manner to give a product of controlled and particularly very fine particle size. Further, this condensation may be carried out in an environment containing a reactive agent which interacts with the product material prior to, during or subsequent to condensation to produce particles of modified physical and/or chemical surface constitution.

Volatilisation of most refractory solids requires temperature above 2000°C and 70

[Price 25p]

SPECIFICATION AMENDED - SEE ATTACHED SLIP



usually beyond 3000°C. Beyond 3000°C there are few solid materials available for containment of the material to be vaporised, but it has been found that the centrifugal liquid wall furnace is eminently suitable for this purpose. In such a furnace, the container is constituted by a tube of suitable material which is fused during operation but which retains its shape by being rotated axially at high speed holding the liquid layers in position by centrifugal force. The liquid wall may be derived from a material other than the refractory which is to be vaporised. Alternatively, the material to be vaporised may itself provide the liquid wall by fusion from a performed tubular core of the refractory.

To vaporise the materials contemplated in accordance with this invention, it is necessary to employ a gas stream not only of high temperature but also of high enthalpy and it has been found that a stream of hot gas, known as a "plasma jet", gives excellent results. Alternatively, a suitable chemical flame augmented by means of electrical power (the "augmented flame") may be used. The plasma jet, with which most of our experiments have been conducted, is produced by a high direct current arc burning continuously between a refractory cathode and a cooled nozzle anode giving rise to a fluid which emerges from the nozzle as an incandescent jet similar in appearance to an oxy fuel flame but usually much brighter. Plasma jets may be produced with inert gases as operating fluids, e.g. argon or helium, but for many applications it is desirable to increase the power of the jet by using a polyatomic gas such as nitrogen, carbon monoxide, hydrogen or ammonia. Use of such gases, or suitable mixtures thereof, has the additional advantage in some cases of entering into chemical reaction with the material undergoing vaporisation. Thus, oxides and other compounds may be reduced to more volatile species, thereby facilitating vaporisation of the material at lower temperatures. Such reactions can also be undertaken by the incorporation of additional substances, e.g. carbon in the refractory core material. For example, this type of reaction can be performed in suitable cases by addition of free metal or carbon to an inorganic oxide core.

The invention may be applied to any refractory material which is amenable to volatilisation, including, for example, refractory oxides such as alumina, zirconia, titania, chromium oxides, thoria, magnesia, silica, manganese oxide, zinc oxide, ceric oxide or precursors of such materials, i.e. materials from which the oxide is readily derived, e.g. oxalates or nitrates.

After volatilisation has occurred, a re-

active gas may be introduced into the gas stream to effect a further chemical reaction. A vaporised oxide, for example silicon monoxide or silicon dioxide, may be converted to a carbide by reaction with a carbon containing gas, such as methane. A vaporised oxide may be converted to the nitride by reaction with ammonia or a mixture of nitrogen and hydrogen. A vaporised lower oxide may be converted to a higher oxide by reaction with air or oxygen. Other high temperature vapour phase reactions may be similarly effected.

The hot vapour so produced is passed immediately to a quenching chamber which conveniently may be in the form of a cooled tube. Radially and/or axially directed gas jets pass into a quenching chamber, the flow rate of gas and the positioning of the jets being designed to control the cooling rate of the vapour and hence the size of the solid particles produced. By suitable selection of the cooling gas, further chemical reactions may be caused to occur at this stage. If quenching is achieved in presence of water vapour, either injected into the cooling zone or produced *in situ* by oxidation of hydrogen derived from the plasma jet, the condensed refractory material may be obtained with a hydroxylated surface which can, in some cases, give rise to thixotropic or other useful properties.

Instead of water vapour, a reactive organic vapour such as an alcohol, e.g. methanol may be fed into the gas stream in a zone after the formation of the first discrete micro-particles of condensed material, but before the aggregation of these particles into clusters. By this means, the reactive gas becomes chemically combined at the surface of the particle so that a core of inorganic material surrounded by a hydrophobic organic layer is obtained. Also particles possessing hydroxylated surfaces, such as silica, prepared by the process described in the previous paragraph can conveniently be reacted before aggregation with organic compounds containing a reactive halogen group e.g. methyl chloride or $(CH_3)_3SiCl$ (trimethyl silyl chloride).

By varying the nature and proportion of the organic reactant or by combining two or more organic reactants, a variety of surfaces may be achieved. It is also possible to employ organic reactants containing suitable protecting groups which may be subsequently removed. In this way, surfaces containing varying proportions of a whole range of reactive groups can be achieved. Thus, these spherical "composite-polymer" particles may be tailored to meet specific needs. The fully alkylated silica particle is of especial interest as a filler for silicone rubbers and other polymers. Micro-particles which are almost completely alkylated but

still contain a small proportion of polar groups, (e.g. $-\text{OH}$, $-\text{NH}_2$, etc.), present a new area of investigation for biological activity, e.g. as antiviral agents.

5 The invention may be put into effect using apparatus illustrated in the accompanying schematic drawing which shows a centrifugal liquid wall furnace connected to a cooling and precipitation section.

10 The furnace comprises a steel tube 1, cooled by circulating water entering 14 and leaving at 15, and into which is fitted a ceramic core 2 of material to be vaporised. The tube 1 and the core 2 together constitute the furnace and connected to the left hand end of the furnace is a plasma jet device 3 into which is incorporated an injection nozzle 4 for injecting fresh raw material into the furnace so as to provide 20 for continuous operation if desired.

The ceramic core 2 is preformed by standard casting techniques; such products are generally sufficiently resistant to thermal shock for the operation of the process. The 25 ceramic core 2 is held in the steel tube 1 in such a manner as to be rotatable, rotational speeds greater than about 500 rpm usually being necessary if the molten ceramic material 5 is to be stabilised by centrifugal 30 force.

The ceramic core 2 is heated convectively by contact with the hot turbulent stream of gas from plasma jet 3. It is not necessary in every case to achieve a temperature in 35 the furnace above the boiling point of the refractory as even a modest temperature can produce continuous vaporisation because the liquid surface is continuously purged by fresh gas. As previously indicated, where continuous operation is required, fresh material is fed through the injector 4, conveniently in the form of powder, pellets, rod or wire.

The quenching section 6, cooled by circulating water entering at 16 and leaving at 45 17, has an inlet portion 7 provided with radially directed tubes 8 for introducing quenching gas. The outlet end 9 of the quenching section is connected to an electrostatic precipitator 10. Conveniently, the gas issuing from the quench section is passed tangentially into a precipitation tube 11 containing a tungsten wire 12 that is electrostatically charged. The lower section 13 50 of the precipitation chamber acts as a collection vessel for the modified inorganic product.

The invention is illustrated by the following Examples:—

60 Examples

1. Silicon monoxide

A furnace core was cast from an equimolar mixture of ground fused quartz and finely ground petroleum coke. A commercial organo-silicate was used as binder. 65

After drying and firing in an inert atmosphere the core weighed 2670 g. This core was heated for 12 minutes in the liquid-wall furnace, using a nitrogen plasma (gas flow 60 litres/minute at S.T.P., plasma 70 power 30 kW). At the end of the experiment the core weighed 2282 g., thus 388 g. were volatilised of which 323 g. comprises the silica evaporated mainly as silicon monoxides. The effluent vapour was rapidly 75 cooled by injection of nitrogen (160 litres/minute) and by passing through a water-cooled tube. The product consisted of a low density yellow-brown powder. Chemical analysis indicated that this contained 80 70% SiO , the remainder consisted of SiO_2 . Electron micrographs showed that the predominant component of the product was a fibrous material of which the fibres were about $0.02\text{ }\mu\text{m}$ in diameter and over $1\text{ }\mu\text{m}$ 85 in length. Many of these fibres were observed to terminate in spherical growths suggesting growth by a vapour-liquid-solid mechanism.

2. Alumina 90

A furnace core was cast using a commercial castable form of alumina (alumina containing a small amount of lime), to which had been added fine petroleum coke in the molar ratio alumina : carbon, 1 : 2. 95 The presence of carbon aided volatilisation in the liquid-wall furnace by formation of the lower oxides of aluminium (e.g. Al_2O , AlO , Al_3O_4). The core was dried and fired in an inert atmosphere after which it weighed 100 3720 g. The core was then heated in the liquid-wall furnace for 15 minutes in a plasma of argon (40 litres/minute at S.T.P.) and hydrogen (40 litres/minute at S.T.P.) with plasma power 30kW. After the experiment the core weighed 2710 g. thus 105 610 g. were volatilised of which 494 g. comprised the alumina evaporated. The hot vapour from the furnace was treated with a stream of air (160 litres/minute) and oxygen (50 litres/minute) which oxidised the 110 lower aluminium oxides to alumina and cooled the gases causing particles to condense. The product consisted of a white powder of low bulk density, which was 115 shown by electron microscopy to consist of spherical particles approximately $0.05\text{ }\mu$ in diameter. X-ray powder photography showed that the powder consisted of a mixture of δ - and γ -alumina. 120-

3. Titania

A furnace core was made in two stages. A thin annular core was made from castable alumina and after firing an inner annular layer was made by casting an equimolar 125 mixture of rutile and finely powdered petroleum coke using a small amount of organosilicate binder. The presence of carbon aided volatilisation of titania in the liquid-wall furnace mainly by forming TiO . 130

After drying and firing in an inert atmosphere the core weighed 3990 g. The core was heated in the liquid-wall furnace for 7½ minutes in a nitrogen plasma (60 litre/minute at S.T.P., plasma power 30 kW). After the experiment the core weighed 3835 g., thus 155 g. were volatilised of which 135 g. comprises the titania evaporated. The hot vapour from the furnace was treated with a stream of air (160 litres/minute) which oxidised the lower titanium oxides and cooled the gases causing particles to condense. The product was a fine powder, shown by electron microscopy to consist of spherical particles of approximately 0.03 µm diameter. X-ray powder photographs indicated that the powder was mainly rutile.

4. Magnesia

A furnace core was again made in two stages. A thin annular core was made from castable alumina and after firing an inner annular layer was made by casting an equimolar mixture of magnesia and finely powdered petroleum coke using an aqueous magnesium chloride binder. The presence of carbon aided volatilisation of magnesia in the liquid-wall furnace by formation of magnesium vapour. After drying and firing in an inert atmosphere the core weighed 3310 g. The core was heated in the liquid-wall furnace for 12 minutes in a nitrogen plasma (60 litres/minute at S.T.P., plasma power 30kW). After the experiment the core weighed 3085 g., thus 225 g. were evaporated of which 173 g. comprises the magnesia evaporated. The hot vapour from the furnace was treated with a stream of air (160 litres/minute) which oxidised the magnesium metal and cooled the gases causing particles to condense. The product was a fine white powder shown by electron microscopy to consist of cubic particles approximately 0.025 µm thickness, joined in chains. X-ray powder photographs indicated that the powder was magnesium oxide.

5. Magnesia

The above experiment was repeated using a magnesia core which contained no carbon. The core was cast as above and after drying and firing the core weighed 3875 g. The core was heated for 12 minutes in the liquid-wall furnace using a plasma of hydrogen (40 litres/minute) and argon (40 litres/minute at a lower of 30kW). After the experiment the core weighed 3770 g., thus 105 g. of magnesia were evaporated. The hot vapour from the furnace was treated with a stream of air (160 litres/minute) which oxidised magnesium vapour and cooled the gases causing particles to condense. The product was again a fine white powder consisting of cubic particles of approximately 0.025 µ thickness as indicated by electron microscopy. X-ray powder photographs

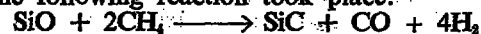
indicated that the powder was magnesium oxide.

The infra-red spectrum of the product dispersed in a disc of potassium bromide showed a strong sharp peak at 3700 cm⁻¹. This peak is characteristic of surface hydroxyl groups on the magnesia.

It may be seen that control of the surface chemistry of the particles may be achieved, and by quenching the vapours in an atmosphere containing water vapour a powder with a high surface hydroxylation may be obtained.

6. Silicon carbide

A furnace core was made as for experiment 1 using an equimolar mixture of ground fused quartz and finely ground petroleum coke. After drying and firing in an inert atmosphere the core weighed 2482 g. The core was heated in the liquid-wall furnace for 8 minutes using a nitrogen plasma (70 litres/minute at S.T.P., plasma power 30 kW). After the experiment the core weighed 2140 g., thus 342 g. were evaporated, of which 285 g. comprises the silica evaporated. During this experiment silicon monoxide distils from the core and from previous experiments the rate of distillation of silicon monoxide throughout the run had been measured. The silicon monoxide content of the furnace effluent being thus known, the vapours were treated on leaving the furnace with two moles of methane gas per mole of silicon monoxide distilled and the following reaction took place:



On cooling the above gas mixture a fine grey powder condensed. This consisted of irregular particles of up to 0.03 µm diameter. X-ray powder photographs showed that the product was predominantly β-silicon carbide contaminated with some silica. Chemical analysis showed that the powder contained at least 70% of silicon carbide.

WHAT WE CLAIM IS:—

1. A process for the production of a finely divided solid which comprises producing a non-volatile inorganic oxide in the vapour phase by heating a melt containing said oxide or a precursor thereof as hereinbefore defined with a gas stream of high temperature and enthalpy, said melt being centrifugally distributed on the inner surface of a hollow rotating body, and subsequently condensing in finely divided form the oxide or a species derived therefrom by physical or chemical modification thereof.

2. A process according to Claim 1, wherein the condensed oxide or species derived therefrom consists substantially of material of particle size less than 2000Å.

3. A process according to Claim 1 or 2, wherein the gas stream of high enthalpy is a plasma jet.



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After drying and firing in an inert atmosphere the core weighed 3990 g. The core was heated in the liquid-wall furnace for 7½ minutes in a nitrogen plasma (60 litre/minute at S.T.P., plasma power 30 kW). After the experiment the core weighed 3835 g., thus 155 g. were volatilised of which 135 g. comprises the titania evaporated. The hot vapour from the furnace was treated with a stream of air (160 litres/minute) which oxidised the lower titanium oxides and cooled the gases causing particles to condense. The product was a fine powder, shown by electron microscopy to consist of spherical particles of approximately 0.03 µm diameter. X-ray powder photographs indicated that the powder was mainly rutile.

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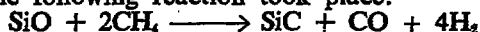
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WHAT WE CLAIM IS:—

1. A process for the production of a finely divided solid which comprises producing a non-volatile inorganic oxide in the vapour phase by heating a melt containing said oxide or a precursor thereof as hereinbefore defined with a gas stream of high temperature and enthalpy, said melt being centrifugally distributed on the inner surface of a hollow rotating body, and subsequently condensing in finely divided form the oxide or a species derived therefrom by physical or chemical modification thereof.

2. A process according to Claim 1, wherein the condensed oxide or species derived therefrom consists substantially of material of particle size less than 2000Å.

3. A process according to Claim 1 or 2, wherein the gas stream of high enthalpy is a plasma jet.

4. A process according to any of Claims 1 to 3, wherein the oxide is incorporated with an additional substance which aids volatilisation.
5. A process according to Claim 4 in which the additional substance consists substantially of carbon.
6. A process according to any of Claims 1 to 5, wherein the oxide is treated with one or more reactive species prior to condensation.
7. A process according to any of Claims 1 to 6, wherein the oxide is treated with one or more reactive species during and/or subsequent to condensation.
8. A process according to Claim 6 or 7, wherein the reactive species is an organic compound.
9. A process according to Claim 6 or 7, wherein the reactive species is water.
10. A process according to any of Claims 1 to 8, wherein the oxide consists substantially of silicon dioxide.
11. A process according to any of Claims 1 to 9, wherein the oxide consists substantially of alumina.
12. A process according to any of Claims 1 to 9, wherein the oxide consists substantially of titanium dioxide.
13. A process according to any of Claims 1 to 9, wherein the oxide consists substantially of magnesia.
14. A process according to any of Claims 1 to 6 in which the oxide is silicon monoxide and the species derived therefrom is silicon carbide.
15. A process substantially as described in any of Examples 1 to 6.
16. Finely divided solids whenever prepared by a process according to any of the preceding claims.
17. Finely divided solids whenever prepared by a process according to Claim 1 and substantially as described in any of Examples 1 to 6.
- R. S. CRESPI,
Chartered Patent Agent,
Agent for the Applicants.

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