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METHOD FOR UTILIZING DETONATION WAVES
TO EFFECT CHEMICAL REACTIONS
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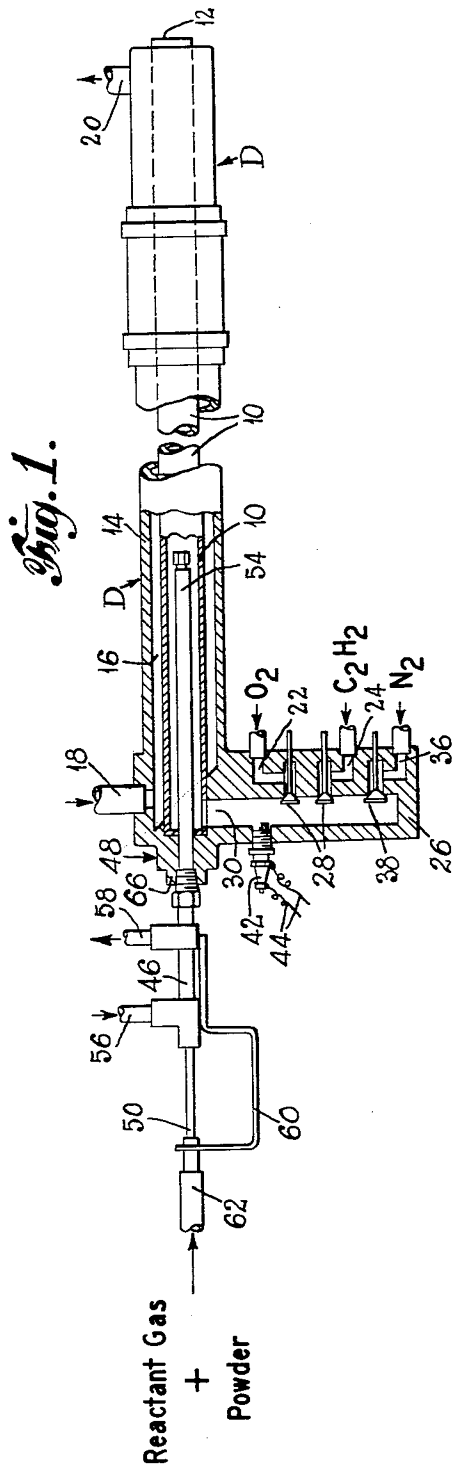
Fig. 1.

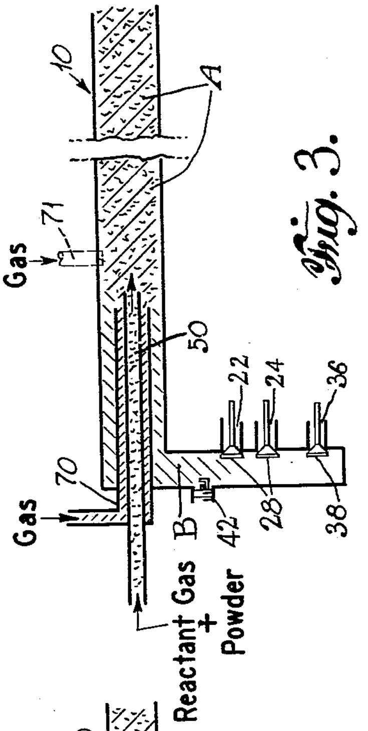
Fig. 3.

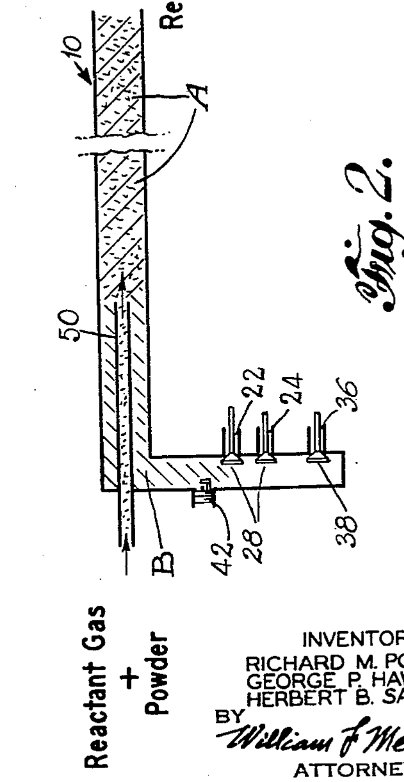
Fig. 2.

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# METHOD FOR UTILIZING DETONATION WAVES TO EFFECT CHEMICAL REACTIONS

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**6 Claims. (Cl. 23—1)**

This invention relates to a method of using detonation waves and for controlling the formation of such detonations. More particularly, it relates to a method for controlling the composition of the reactive gases at different points within a detonation apparatus.

By the term "detonation" is meant a very rapid burning or other exothermic reaction in which the flame front moves through the unburned material at velocities higher than the velocity of sound in the unburned material, and therefore characterized as supersonic velocities. (Typical calculated velocities of sound at normal pressure are 1085 feet per second at 18° C. in a 50% oxygen-50% acetylene mixture, 1384 feet per second in the same mixture at 200° C. and 1122 feet per second at 18° C. in a 9.5% acetylene-90.5% air mixture.) The rate of flame propagation is far greater in a detonation than in a deflagration, which is a burning or other exothermic reaction in which the velocity of flame propagation does not exceed the velocity of sound in the unburned material. According to Wilhelm Jost's "Explosion and Combustion Processes in Gases," McGraw-Hill Book Co., Inc., New York (1946), pages 160 to 210 of which are devoted to detonations in gases, the velocity of the flame front in gas detonations thus far investigated is from 1 to 4 kilometers per second (about 3,280 to 13,120 feet per second), as compared to, for instance, 50 feet per second for a typical deflagration.

Once a detonation wave has been established in a gaseous medium in a long tube, it travels at a constant velocity. However, except in the special case where the initiation is by a shock wave source, the detonation wave is not established immediately, but only after the flame has travelled some distance as a deflagration. The region through which the flame travels before its transition to detonation occurs will be called the predetonation region.

Heretofore, apparatus has been proposed for utilizing detonation waves and associated phenomena to impart energy to powders provided in a detonatable fluid body to propel said powders at high temperatures and velocities against the surface of a body to be coated. Such apparatus, disclosed and claimed in application Serial No. 275,332, filed March 7, 1952, by R. M. Poorman et al., issued on August 2, 1955, as U.S. Patent No. 2,714,563, is termed a "detonation gun" and comprises an elongated barrel having an open end, means for introducing a detonatable body of detonatable fluid into said barrel, means for providing powder material in said detonatable body of detonatable fluid in said barrel, means for controlling the supply of fluid fuel and oxidant of said detonatable fluid, and a mixing and ignition zone at the rear of the barrel including ignition means for igniting said detonatable fluid in said barrel. The powdered material is carried into the barrel either through the fuel gas stream, oxidant stream, or by a separate stream which introduces the powdered material into the stream of detonatable fluid mixture which carries it into the barrel of the detonation gun.

An improved detonation gun is disclosed and claimed in U.S. Patent No. 2,774,625. This improved detonation gun employs a powder injection tube projecting axially into the gun barrel to introduce the powder into the barrel downstream from the zone in which the detonation is

established. Improved operating results are thus provided since the powder is symmetrically disposed in the cross-section of the barrel and does not build-up deposits in one area of the wall as when introduced from the side of the barrel, and at the same time avoids fouling the mixing and ignition zone with particles as when introduced through that zone.

The above apparatus and associated processes have been used to produce coatings, to spheroidize particles, to clean or roughen surfaces, and to pulverize frangible material.

It has now been found that the unusual conditions of pressure and temperature existing in a detonation make this phenomenon ideal for the promotion of chemical reactions as well as for improved coating processes.

The temperature, gas velocity, ignition characteristics and composition of the products of a detonation wave are determined primarily by the composition of the detonatable material. When an acetylene-oxygen mixture is used, the highest flame velocity and temperature are attained at an oxygen/carbon atomic ratio of 1.0. This mixture is carbon rich or oxygen deficient with relation to stoichiometric amounts for complete combustion to carbon dioxide and water. Therefore, detonation of this particular fuel-oxidant mixture results in an atmosphere that is slightly carburizing or reducing toward many substances. Also there is no appreciable free carbon in the combustion products allowing the walls of the ignition chamber and of the barrel to remain clean and free of carbon deposits. Furthermore the transition of the flame from the original deflagration to the desired detonation takes place rapidly and in a short distance thus producing a relatively small predetonation region.

If the detonation is to be the primary source of a carburizing or reducing reaction, for example, the oxygen/carbon atomic ratio of an acetylene-oxygen mixture should be reduced below 1.0. Under these conditions the transition of the flame from the deflagration to the detonation form may be delayed so much that the desired reaction conditions are not attained in the reaction zone. Also carbon and gummy materials from the incomplete combustion tend to deposit on the walls of the detonation chamber in the predetonation region of the barrel. Little or no deposit occurs downstream of the predetonation region because all material in this downstream region is pushed forward by the forces in the detonation wave. Deposits of carbonaceous material in the predetonation region of the barrel interfere with the operation and make frequent cleaning necessary. Moreover, if the reaction product is a coating, these solid deposits become detached from the wall and are deposited in the coating itself, seriously lowering the quality of the coating.

If it is desired to use a detonation reaction for oxidation, the oxygen/carbon atomic ratio should be increased above 1.0 for an oxygen-acetylene mixture. Here again the ignition characteristics of the mixture may not be as desired; that is, the predetonation region may be too large to enable proper reaction conditions to be obtained and gummy deposits may result.

When acetylene alone or another detonation mixture, such as hydrogen-oxygen or propane-oxygen, for example, is used as the source of the detonation waves for chemical reaction, similar problems are faced. In general the best oxygen/carbon atomic ratio for producing the desired reaction conditions (temperature and product composition, for example) is not the same as the best oxygen/carbon ratio for early establishment of a detonation. Both of these desired composition ratios can be attained by having in the ignition zone a gas composition best for early establishment of a detonation and introducing other components into the gas downstream of the ignition zone to produce the desired reaction conditions in a reaction zone.

It is, accordingly, an object of the present invention to promote chemical reactions by means of the detonation gun process.

An additional object is to improve operating efficiency of the detonation gun by providing specially controlled combustion zones in the various areas of the gun. Specifically, the composition of the detonation gas mixture is desirably varied to provide a method for readily oxidizing or carburizing metal or other materials in the detonation gun.

Other aims and advantages will be apparent from the following description and appended claims.

It should be noted that the material being treated in the reaction zone is not capable itself of sustaining a detonation. The detonation wave must be propagated by the gases surrounding the reactant material being treated in the reaction zone. The material being treated should preferably be a solid or liquid in order to obtain maximum amount of material in the reaction zone in a given time. However, gaseous reactant materials can also be treated.

The invention will be more particularly described with reference to the accompanying drawings in which:

FIG. 1 is a schematic view of a detonation gun in which the method of the invention may be practiced;

FIG. 2 is a diagrammatic view of the device of FIG. 1; and

FIG. 3 is a diagrammatic view of another device in which the invention may be practiced.

The method of this invention is carried out in a detonation gun having an elongated barrel. The barrel has a length-to-diameter ratio sufficiently high to permit the establishment and propagation of a detonation therein. A mixing and ignition chamber directly and continuously connects with one end of the gun barrel and functions to mix and pass to the gun barrel the gases comprising the detonatable body, such as oxidant and fuel gases. Conduit means and valves are provided to introduce the gases into the ignition and mixing chamber. Means are provided to introduce material to be acted upon by the detonation, such as comminuted solid material, into the fuel gas and oxidant gas mixture in the gun barrel. Means are also provided in the mixing and ignition chamber to ignite the gas mixture therein and to establish the detonation in the gun barrel. The oxidant-fuel mixture can be varied to give desired detonation properties. The improved method of operation of the present invention comprises maintaining the oxidant gas-fuel gas mixture in the ignition and mixing chamber and in the portion of the barrel upstream of the entry for powder or other reactant so as to provide desired characteristics of ignition and detonation formation, and modifying the oxidant gas-fuel gas mixture in the downstream reactive portion of the barrel to the composition there desired by concurrently introducing an additional and separate quantity of reactive hydrocarbon, oxidant gas or other reactant into the reaction portion of the barrel.

More specifically, an oxidant reaction gas, such as oxygen, may be added to the detonatable gas mixture in the reaction zone to effect more oxidizing conditions during the combustion reaction; or, by the addition of a hydrocarbon fuel gas at that point, the combustion reaction may be made more carburizing.

Through utilization of this method, it has been possible to obtain desired combustion in the ignition zone, and the fuel gas mixture provided in the downstream portion may be chosen for maximum carburizing efficiency in reacting with the oxidant gas and the powder. For example, ethylene may be utilized rather than additional acetylene to adjust the oxidant/fuel gas ratio.

In FIG. 1, detonation gun D is provided comprising an elongated barrel **10** having an open end **12** from which the products of the detonation and powders pass to the object to be coated or from which reaction products are removed. Cooling water circulating jacket **14** is provided around barrel **10** to prevent overheating. Cooling water is supplied to the annular space **16** between jacket **14** and barrel **10** through inlet means **18**, and water passes from annular space **16** through outlet means **20**.

Oxidant and fuel are supplied to port means **22** and **24**, respectively, of mixing block **26** which is provided with poppet valves **28** for regulating the flow of such fluids at timed intervals. Mixing of the fuel and oxidant takes place in mixing and ignition zone or chamber **30** of mixing block **26** and the detonatable mixture is passed to barrel **10** of the detonation gun D. Mixing block **26** is also provided with purging gas inlet port means **36** and poppet valve means **38** for purging mixing chamber **30** and barrel **10** of gases in the intervals between each successive detonation and the introduction of the following detonatable charge into elongated barrel **10** of the detonation gun.

Means are provided in the walls of mixing chamber **30** for insertion of ignition means **42**, such as a spark plug or the like, into the mixing chamber; and energizing lines **44** are also provided.

Reactant entry tube assembly **46** passes through the rear or breech end **48** of cooling water jacket **14** and the elongated barrel **10** and passes axially through the barrel to a point downstream of the zone (in the region of ignition means **42**) where ignition occurs and downstream of the point where the establishment of the detonation phenomenon occurs. The powder entry tube assembly **46** preferably comprises powder entry tube **50**, cooling jacket **54** surrounding entry tube **50** over at least that portion of entry tube **50** which is positioned in the interior or barrel **10**, cooling fluid inlet and outlet parts **56** and **58** respectively, and guide bracket means **60** for properly supporting entry tube **50** to prevent bending or breakage. Entry tube **50** is supplied with reactant gas and powder by a line **62**.

When at least one of the materials to be treated in the detonation apparatus is a powder, a suitable powder dispenser is employed for suspending the material in a gas stream in which it is carried into the barrel **10** of the detonation gun.

In all the figures, the same reference numerals refer to the same apparatus elements.

FIG. 2 shows the two gas concentration zones A and B capable of provision in accordance with the instant invention. Zone A represents the reaction portion of the gun barrel where the material to be treated is injected. In this portion, the oxygen/fuel gas ratio is maintained at a value so as to provide the desired chemical action. Zone B is the mixing, ignition and predetonation zone, wherein the oxygen/fuel gas ratio is maintained at a value to provide desired ignition and detonation promotion.

The oxygen-carbon atomic ratio in zone A can be maintained at a value different from that in zone B by introducing to zone A an oxidant or hydrocarbon. This reactant gas is conveniently introduced through tube **50**. When a powder is to be treated in the detonation gun, the reactant gas can act as the powder carrier gas or as a replacement for part of the powder carrier gas. This result may, however, be accomplished by other means such as a third auxiliary gas inlet either parallel or perpendicular to the gun barrel axis.

FIG. 3 shows such auxiliary gas entry means. Gas entry tube **70** is concentric with reactant entry tube **50** thus introducing the desired amount of oxidant or hydrocarbon into zone A of the gun barrel. Tube **71**, in broken lines, shows the alternative method for introducing the auxiliary gas into zone A.

This invention has several uses; the first being a method by which chemical reactions are promoted through use of detonations and in which the desired oxidizing or reducing conditions can be obtained by varying the detonation mixture in the reaction zone.

The second use being a method by which the detonatable gas mixture in the gun barrel can be varied advantageously in composition along the length of the gun barrel. This has been accomplished by introducing active gases through the reactant feed tube, thus, producing two gas zones in the gun barrel whose compositions are different. If more than one auxiliary gas supply tube or station were used, the composition of the fuel could be varied in many steps or nearly continuously along the barrel length.

The reaction of solid and liquid particles with the products of detonation of the gas in which they are suspended is surprisingly rapid, perhaps because of the very high relative velocity between particle and gas, leading to high rates of transfer of heat and material. The velocity of the detonation products of equimolar acetylene-oxygen mixture in respect to particles originally at rest in the unreacted gas mixture is calculated to be 1200 meters/sec. initially. This relative velocity decreases, of course, as the particles are accelerated.

The following examples serve to illustrate different types of reactions that can be promoted by means of a detonation process in which the reaction zone conditions are different from the ignition zone conditions. It is apparent that other reactions of similar nature can also be carried out. Detonation gun apparatus of the type shown in FIG. 1 was used for all the examples.

## EXAMPLE I

*Carburization of tungsten*

Acetylene at 3.02 c.f.m. and oxygen at 2.94 c.f.m. (O/C ratio of 0.97) were fed into the detonation gun. Tungsten powder (average size 4.5 microns) was fed at a rate of about 6 lbs. per hour entrained in an ethylene gas stream of 0.4 c.f.m. through the axial feed tube. The oxygen/carbon atomic ratio in the reaction zone was 0.86. The gun was operated at about 4 detonations per second with attendant nitrogen purge. The product was collected as a coating and analyzed to contain tungsten carbide ($W_2C$).

The exact method by which carbon is transferred from the gas to the metal is believed to be similar to the mechanism which occurs in the carburization of steel. The carbon bearing gas is thought to decompose on the surface of the hot particles and the carbon, then to diffuse into and react with the particles. Since most metals, including tungsten (melting point of 3370° C.), melt when exposed to an oxygen-fuel detonation in the detonation gun, and the diffusion of carbon is very rapid in a molten metal, it can be seen how appreciable amounts of carbon can be added readily to metal powders during the detonation.

The use of ethylene as the powder carrier gas, tungsten powder (0–10 micron in size) plus 16% cobalt binder (0.44 micron in size), and an oxygen/fuel gas ratio in the ignition zone of about 1.0 provides a tungsten carbide coating with useful hardness, grindability and wear resistance properties.

## EXAMPLE II

*Reduction of iron oxide (N.B. 478–133*

Oxygen gas at 2.75 c.f.m. and propane at 1.0 c.f.m. were fed into a detonation chamber to form a detonation mixture having an oxygen/carbon atomic ratio of 1.8. $Fe_2O_3$ powder at a rate of about 10 grams per minute was introduced downstream of the predetonation region in a 0.61 c.f.m. propane carrier stream. The oxygen/carbon ratio in this downstream reaction section was 1.1. The detonation mixture was ignited about 4 times per second with attendant nitrogen purge. The powder product was collected at the equipment outlet. This powder contained 74.3 wt. percent Fe, 19.1 wt. percent O and 1.92 wt. percent total C.

## EXAMPLE III

*Reduction of iron oxide (N.B. 478–135)*

Oxygen at 3.3 c.f.m. and 1.25 c.f.m. propane were fed into a detonation chamber to form a detonation mixture having an oxygen/carbon atomic ratio of 1.8. $Fe_3O_4$ powder at about 10 grams per minute was introduced downstream of the predetonation region in a propane carrier stream of 0.61 c.f.m. The oxygen/carbon atomic ratio in this downstream reaction zone was 1.2. The detonation mixture was ignited about 4 times per second with attendant nitrogen purge between detonations. A powder product was collected at the outlet of the reaction chamber which contained 77.6 wt. percent Fe, 16.3 wt. percent O and 1.96 wt. percent total C.

## EXAMPLE IV

*Carburization of molybdenum (Run 2B–3299)*

Oxygen at 3.36 c.f.m. and 3.14 c.f.m. acetylene were fed into a detonation gun to form a detonation mixture having an oxygen/carbon atomic ratio of 1.07. A powder mixture of molybdenum and 20 wt. percent Type 302 stainless steel binder was introduced in a 0.4 c.f.m. ethylene carrier gas downstream of the predetonation region. The oxygen/carbon atomic ratio in this downstream reaction zone was 0.95. The detonation mixture was ignited about 4 times per second with nitrogen purge between detonations. The powder was propelled out of the detonation gun and impinged on a steel baseplate to produce a molybdenum carbide coating containing 82.2 wt. percent Mo, 4.66 wt. percent total C and 0.19 wt. percent free C.

A wide variety of reactive gases may be employed for modifying the composition of the detonatable mixture in the reaction zone. In addition to propane and ethylene disclosed above, acetylene, ethane, methane, butane could be used to increase reducing and carburizing action. Oxygen could also be added to increase oxidizing action.

In addition to solid reactant materials being treated by the detonation as described above, liquid and gaseous materials could be used. For example, liquid or vaporous silicon tetrachloride could be injected into an oxidizing detonation mixture and be converted to silica.

What is claimed is:

1. In the method of effecting a chemical reaction such as oxidation, reduction and carburization by directing a detonation wave against a comminuted solid reactant to produce a reaction product, wherein a predetermined ratio of fuel to oxidant in an ignition zone produces optimum flame velocity and temperature in said detonation wave, and wherein the atmosphere resulting from said detonation is not the optimum for effecting an efficient chemical reaction of said comminuted solid reactant, the improvement comprising adding a supplemental reactive gas in a reaction zone adjacent to the ignition zone to modify the detonatable composition in said reaction zone to suit the desirable reaction conditions for said comminuted solid reactant, thereby promoting the chemical reaction of said comminuted solid reactant and increasing the yield of reaction product.

2. A method according to claim 1, said comminuted solid reactant being substantially uniformly incorporated in said supplemental reactive gas.

3. A method according to claim 1, said supplemental reactive gas being present in the detonatable composition in said reaction zone in such amount as to render the subsequent detonation reaction more oxidizing whereby the reaction product is substantially correspondingly oxidized.

4. A method according to claim 1, said supplemental reactive gas being present in the detonatable composition in said reaction zone in such amount as to render the subsequent detonation reaction more reducing whereby the reaction product is substantially correspondingly reduced.

5. The improved method of operating a detonation gun including an ignition chamber and gun barrel which comprises the steps of introducing into the ignition

chamber and gun barrel of the gun, the detonatable fuel gas-oxidant gas mixture of acetylene and oxygen respectively having an oxygen/carbon atomic ratio of about 1/1, introducing downstream in the gun barrel with respect to said ignition chamber a charge of comminuted solid material and at the same time, introducing an additional and separate quantity of a hydrocarbon gas in quantity sufficient to provide a fuel gas-oxidant gas detonatable mixture in said downstream portion of the gun barrel having an oxygen/carbon atomic ratio less than that in the ignition chamber, and igniting the detonatable fuel-oxygen mixture in said ignition chamber.

6. A process for promoting chemical reactions such as oxidation, reduction and carburization of comminuted solid reactant material by detonation which comprises forming a detonatable gas body in an ignition zone, introducing into a reaction zone contiguous with the ignition zone a detonatable gas body having different overall composition from the detonatable gas body in the ignition zone, said reaction zone detonatable gas body having proper oxidation-reduction characteristics for promoting the desired chemical reactions, introducing comminuted solid reactant material into the reaction zone to be acted upon by the reaction zone detonatable gas body, and igniting the detonatable gas body in the ignition zone whereby a detonation wave is formed which passes through the reaction zone, causing the comminuted solid reactant material to take part in a chemical reaction under optimum conditions.

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