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AEROSOLS

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This invention relates to improved methods for producing dispersions of finely divided solids in air.

Solid aerosols, dispersions of finely divided solids in air, have previously been prepared by various methods. One such method consists in subjecting a finely divided solid to the burst of an explosive. This method, however, is not satisfactory for the dispersal of materials which are sensitive to heat since the burning of the explosive generates a large quantity of heat which in turn decomposes the material being dispersed. Another known method is the generation of aerosols from solutions of solids in low boiling liquids by forcing such solutions through nozzles in continuous stream into the air. This method is satisfactory only for dispersing solids which are soluble in suitable low boiling liquids, and cannot be used for the dispersing of insoluble materials. Moreover, this method of spraying solutions from nozzles is not suitable for the generation of aerosols in difficultly accessible locations.

This invention has as an object the provision of an improved method for dispersing finely divided solids in air. A further object is to provide a process for generating solid aerosols whereby dispersion is effected without thermal decomposition of the material being dispersed. A still further object is the provision of a process for generating solid aerosols in difficultly accessible locations. Additional objects will become apparent from an examination of the following description and claims.

These and other objects and advantages are accomplished according to the hereindescribed invention which broadly comprises the process for the preparation of solid aerosols by subjecting a finely divided solid material to a single, explosive, disruptive burst in which no heat is generated. In a more restricted embodiment this invention comprises bursting in the air a receptacle containing a finely divided solid material and a fluid having a vapor pressure of at least three atmospheres at 25° C., said fluid having the property of expanding endothermally, being a non-solvent for said solid material and being under a pressure of at least three atmospheres in said receptacle.

In a still more restricted embodiment this invention comprises bursting in the air a receptacle containing a solid material having a particle size of less than 20 microns weight median diameter and a fluid having a vapor pressure of at least 10 atmospheres at 25° C., said fluid having the property of expanding endothermally, being a non-solvent for said solid material and being under a pressure of at least 10 atmospheres in said receptacle.

In a still more restricted embodiment this invention comprises bursting in the air a closed receptacle containing a solid material having a particle size of less than 10 microns weight median diameter and a fluid having a vapor pressure of at least 20 atmospheres at 25° C., said fluid having the property of expanding endothermally, being a non-solvent for said solid material and being under a pressure of at least 20 atmospheres in said closed receptacle.

One preferred embodiment of this invention comprises bursting in the air a closed receptacle containing carbon dioxide under a pressure of at least 20 atmospheres and a protein, e.g., blood albumin, egg albumin, gliadin, zein, casein, or the like, having a particle size of less than 10 microns weight median diameter.

Another preferred embodiment of this invention comprises bursting in the air a closed receptacle containing carbon dioxide under a pressure of at least 20 atmospheres and an insecticide, e.g., pyrethrum, rotenone, ferric dimethyl dithiocarbamate, p,p'-dichlorodiphenyltrichloroethane, dodecyl thiocyanate, lead arsenate, calcium arsenate, sulfur, basic copper carbonate, barium fluosilicate, calcium fluosilicate, or the like, having a particle size of less than 10 microns weight median diameter.

Various arrangements and selections of equipment for the operation of my process are possible. In one preferred arrangement the solid material to be dispersed having a particle size of less than 10 microns weight median diameter, said material being treated with about 1% of its weight of a surface-active agent which reduces cohesion between the particles, is placed within a container capable of being ruptured. A low-boiling liquid or gas which is a non-solvent for the finely divided solid material and which has a vapor pressure of at least 20 atmospheres at 25° C., is then placed under a pressure of at least 20 atmospheres in the closed container. The charged container after being placed in the locality where the aerosol is to be generated, is burst or ruptured or shattered by appropriate means whereby the finely divided solid is dispersed into an aerosol by the resultant single, endothermic, disruptive burst of the compressed gas or low-boiling liquid.

The following examples, in which proportions are in parts by weight unless otherwise specified, are given for illustrative purposes and are not intended to place any restrictions on the hereindescribed invention.

Example I

A cylindrical steel vessel fitted with a capillary inlet for gas and a shear disc head and having a capacity of about 7.5 cc. is charged with 1.98 grams of egg albumin which has been ground in a ball mill until the particles have a weight median diameter of 6.6 microns and 76% (by weight) have a diameter of less than 10 microns. The opening in the head is closed by discs of cellulose acetate of sufficient aggregate thickness to require a pressure of about 700 lbs./sq. in. to rupture them. Carbon dioxide is admitted through the capillary inlet until the internal pressure is sufficient to rupture the closure. The rupture of the closure is accompanied by an explosive eruption of the contents with the formation of an egg albumin aerosol without the generation of heat. Determination of the mass concentration of solid particles in the aerosol carried out on three concordant runs, by the method described below, indicates that on an average 64%, 39% and 27% of the theoretical amount (the total weight of the solid originally used for the preparation of the aerosol) of egg albumin remains suspended in the air for periods of one to five, six to ten and eleven to fifteen minutes, respectively, after the rupture of the vessel.

The aerosol is generated in a closed chamber approximately 10 ft. x 10 ft. x 10 ft. in dimensions at a point approximately 2 feet below the geometric center of the chamber. A circulating fan placed directly below the aerosol generating apparatus is run at a rate which circulates 1500 cu. ft. of air per minute to obtain a uniform distribution of the aerosol in the test chamber. This chamber contains a set of nine Pyrex glass tubes filled

with Pyrex glass wool carefully placed to eliminate channels without packing to the point of high resistance, each of which has been dehumidified by drawing through it over an eight-minute period 1.4 cu. ft. of air which has been dried by calcium chloride. These tubes are arranged in three sets of three each on a vertical frame which stands two feet away from the center of the floor of the chamber. In each set of three, one tube is placed horizontally at each of three levels (½ ft., 5 ft. and 8 ft.) from the floor of the chamber. Each set of three tubes (A, B and C) is attached to a branching vacuum line of rubber tubing, the single end of which leads through the chamber wall to an individual stopcock on a vacuum manifold. The vacuum line leads from the manifold through a dry test meter which is provided with dials for reading gas volumes in decades from 1/100 of a cubic foot upward. The vacuum source is an air pump with capacity of 3 cu ft. of air per minute. A differential manometer is attached to the vacuum line side of the meter so that the meter reading can be corrected to atmospheric pressure. Exactly one minute after the generation of the aerosol the circulating fan is stopped and filtration of the aerosol through Set A of the filter tubes is begun. Sampling through Set A is terminated at 5 minutes and Set B and Set C are used in the same way during the intervals six to ten minutes, and eleven to fifteen minutes, respectively, after the generation of the aerosol. Gas meter readings are obtained before and after each filter period and manometer readings during each one. The filter tubes are again dehumidified before removal from the filter positions by drawing dry air through all nine tubes at the rate of 1.6 cu. ft. per minute for eight minutes. The tubes are then removed and stoppered, carefully wiped with a clean chamois, and weighed. In calculating the mass concentration of the aerosol from these measurements, the volume of air passed through the filter is first calculated by the formula:

$$V_0 = 28.3V \times \frac{B-M}{B}$$

where V is the volume in cubic feet recorded by the meter, B is the barometer reading in mm. of mercury, M is the manometer reading in mm. of mercury, and V_0 is the corrected volume of filtered air in liters. The mass concentration is calculated by dividing the weight gain for each set of filters by the volume of air (V_0) passed through the set.

Settling rates calculated from these data indicate that the average size of the aerosol particles is about 17 microns. The settling law on which these calculations are based is:

$$\frac{dC}{dt} = -\frac{Cv}{h}$$

wherein C is the mass concentration, v is the velocity of sedimentation calculated from Stokes' law, t is the time and h is the height of the chamber. By combining the integrated form of this equation with Stokes' formula the following expression for the average diameter d is obtained:

$$d = \sqrt{\frac{18\eta h \ln C_a/C_b}{g\rho t}}$$

wherein η is the coefficient of viscosity of the gaseous medium, h is the height of the chamber, C_a and C_b are the average mass concentrations of the solid in the gaseous medium a and b minutes, respectively, after the burst, g is the acceleration of the solid body due to gravitation, ρ is the density of the solid material and t is the time. Using the values η (viscosity of air) $= 1.86 \times 10^{-4}$ poises, $h = 250$ cm., g (acceleration) $= 981$ cm. per sec. per sec.,

the following expression for the average diameter D in microns is obtained:

$$D = 18.3 \times \sqrt{\frac{\log C_3/C_{13}}{\rho}}$$

where C_3 is the average mass concentration of solid in air during the period one to five minutes after the burst, C_{13} is the average mass concentration of solid in air for the period eleven to fifteen minutes after the burst, and ρ is the density of the solid.

Example II

A glass ampoule having a volume of about 50 cc. is loaded with 22 grams of solid carbon dioxide and the tube evacuated and sealed. The cold ampoule is placed in an axial position in the center of a paper cylinder containing 22 grams of finely divided lithopone, having an average particle size of about 0.5 micron diameter and which has been coated with 1% of its weight of the coconut oil soap available commercially under the trade name Distolene. The lower end of the glass ampoule projects below the end of the outer paper cylinder and the upper portion of the ampoule projects above the paper cylinder. Vanes are attached to the upper end of the ampoule to control the direction in which it falls in air. After allowing the container to warm up to room temperature it is allowed to drop onto a hard surface, whereupon it explodes violently producing a cloud of smoke composed of finely divided lithopone.

Example III

One thousand grams of zinc oxide having an average particle size of about 0.2 micron diameter, which is available commercially as a pigment grade of zinc oxide, 5000 g. of water and 10 g. of diethylene glycol monolaurate are passed through a colloid mill until a uniform slurry is obtained, fifteen minutes being required. The resulting surface treated zinc oxide is filtered from the water, dried at 115° C. and passed through a Micronizer to disintegrate the filter cake into individual solid particles. The gas bomb with shear disc head of Example I is charged with 2.83 g. of the resultant zinc oxide having a particle size of about 0.2 micron diameter surface treated with 1% of its weight of diethylene glycol monolaurate. After closing the bomb with cellulose acetate discs, carbon dioxide gas is introduced until the internal pressure is sufficient to rupture the cellulose acetate closure, this being about 700 lbs./sq. in. Mass concentration data obtained for the zinc oxide aerosol produced indicate that, on the average, 32%, 26% and 17% of the theoretical amount of solid remains airborne for periods of one to five, six to ten and eleven to fifteen minutes, respectively, after the generation of the aerosol.

In addition to the specific methods of dispersing finely divided solids described in the examples, other modifications of the general process of this invention involving the use of a single, endothermic, disruptive burst may be used. For example, the finely divided solid particles may be placed in a container made of glass or other frangible material together with solid carbon dioxide, the container closed and the contents allowed to come to room temperature with liquefaction of the carbon dioxide, and the vessel then ruptured by external means.

While this invention has been illustrated with particular reference to the formation of aerosols of egg albumin, lithopone and zinc oxide, it is to be understood that said invention is generic to all finely divided solid materials. Included among aerosols which may be had in accordance with this invention are those of cornstarch; yeast; proteins, e.g., blood albumin, egg albumin, gliadin, zein and casein; organic and inorganic insecticides, e.g., pyrethrum, rotenone, ferric dimethyl dithiocarbamate, p,p'dichlorodiphenyltrichloroethane, dodecyl thiocyanate, lead arsenate, calcium arsenate, sulfur, basic copper carbonate, barium fluosilicate and calcium fluosilicate; white pigments and

pigment extenders, e.g., zinc oxide, white lead, lithopone, barium carbonate, barium sulfate, clay, calcium carbonate and aluminum silicates; colored pigments, e.g., chrome yellow, basic zinc chromates, phthalocyanine blue, cadmium yellow, red iron oxide, carbon black and the like. The novel process of this invention is particularly well adapted for the provision of aerosols of insecticides and proteins.

It is to be understood that the finely divided solid materials dispersed in accordance with this invention should have a particle size of less than 20 microns weight median diameter. Optimum results are obtained when said material has a particle size of less than 10 microns weight median diameter. By "weight median diameter," as employed herein and in the appended claims, it is meant that the amount by weight of the solid material particles having a diameter less than the specified diameter equals the amount by weight of said particles having a diameter greater than said specified diameter.

The dispersibility of the solid particles may be improved, if desired, by treating them with a material which reduces cohesion between them, e.g., by coating said particles with about 1% by weight of a surface active material. Examples of such surface-treating agents which are particularly effective include diethylene glycol monolaurate, mannitan monolaurate and soya lecithin. The presence of such surface-treating agents is not, however, essential to the production of aerosols according to the method of this invention.

While this invention has been illustrated with particular reference to the use of carbon dioxide as dispersant, it is contemplated that any substance which is a non-solvent for the solid material being dispersed, which has a vapor pressure of at least three atmospheres at 25° C., and which expands endothermally, is operative. In other words, any compressed gas or low-boiling liquid which is chemically inert toward, and is not a solvent for, the finely divided solid being dispersed, which has a vapor pressure at 25° C. of at least three atmospheres and which expands endothermally, may be used to provide the disruptive force. Included among examples of said substances are carbon dioxide, carbon monoxide, ammonia, sulfur dioxide, nitrogen, acetylene, oxygen, air, ethane, ethylene and methyl chloride, it being understood, of course, that in every instance the substance used to provide the disruptive force is one which is inert toward, and a non-solvent for, the finely divided solid being dispersed. As hereinbefore stated, the substance employed as a vehicle for the finely divided solid, i.e., the substance used to provide the endothermic disruptive burst, should have a vapor pressure of at least three atmospheres at 25° C. Markedly improved results are obtained when said substance has a vapor pressure of not less than ten atmospheres at 25° C., while optimum results are had when said substance has a vapor pressure of twenty atmospheres or more at 25° C.

The disruptive substance contained in the receptacle should be under a pressure of at least three atmospheres at the moment of bursting. Improved results are obtained when said substance is under a pressure of not less than 10 atmospheres, while maximum results are had when said substance is under a pressure of at least 20 atmospheres at the moment of the bursting of said receptacle. The only known maximum pressure is that which the container is capable of withstanding. The optimum pressure employed in any given instance depends to a marked degree on the particular type of solid being dispersed, a light fluffy solid requiring less pressure than a more compact one.

Because of the endothermic nature of the disruptive force of this invention, it is particularly useful for the generation of aerosols of finely divided solids which are susceptible to decomposition by heat. It is particularly useful for the preparation of aerosols composed of proteins or insecticides.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that I do not limit myself to the specific embodiments thereof except as defined in the appended claims.

Having described the present invention, the following is claimed as new and useful.

1. The process for obtaining an aerosol, which comprises bursting in the air a frangible receptacle containing a finely divided solid material and a fluid, said fluid in liquid phase having a vapor pressure of at least three atmospheres at 25° C., having the property of expanding endothermally, being inert toward, and a non-solvent for, said solid material and being under a pressure of at least three atmospheres in said receptacle.

2. The process for obtaining an aerosol, which comprises bursting in the air a frangible receptacle containing a solid material having a particle size of less than 20 microns weight median diameter and a fluid, said fluid in liquid phase having a vapor pressure of at least 10 atmospheres at 25° C., having the property of expanding endothermally, being inert toward, and a non-solvent for, said solid material and being under a pressure of at least 10 atmospheres in said receptacle.

3. The process for obtaining an aerosol, which comprises bursting in the air a closed frangible receptacle containing a solid material having a particle size of less than 10 microns weight median diameter and a fluid, said fluid in liquid phase having a vapor pressure of at least 20 atmospheres at 25° C., having the property of expanding endothermally, being inert toward, and a non-solvent for, said solid material and being under a pressure of at least 20 atmospheres in said closed receptacle.

4. The process according to claim 3 wherein the solid material comprises an insecticide.

5. The process according to claim 3 wherein the solid material comprises a pigment.

6. The process according to claim 3 wherein the solid material comprises a protein.

7. The process for obtaining an aerosol, which comprises bursting in the air a closed frangible receptacle containing carbon dioxide under a pressure of at least 20 atmospheres and a solid material having a particle size of less than 10 microns weight median diameter, said solid material being inert toward and insoluble in carbon dioxide.

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