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SLOW-BURNING POWDER FOR FUSES, ETC.

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This invention relates to fuses and, more particularly, to safety or blasting fuses, such as are employed for the delayed firing of bodies of explosive in mining, quarrying, construction and like fields. In general, however, it relates to all fuses, whether in the field of ordnance, of blasting, of pyrotechnics, or elsewhere. The invention consists in a modification of the composition of black powder, in consequence of which such fuses may be improved in safety and in the accuracy of their functioning. This application is in part a continuation of an application filed by me September 11, 1934, Serial No. 743,555.

A safety fuse or blasting fuse includes as its essential feature an elongate body of combustible material which, being ignited at its proximate end, burns gradually, and at length imparts to a body of explosive situated adjacent its remote end the desired ignition. The material originally, and still chiefly, employed as the material for such a fuse is essentially black powder.

There are difficulties and inadequacies incident to the use of black powder for this purpose, such as to have caused a great deal of study and experimentation; but, for all that, no adequate and satisfactory substitute for black powder has been found. The difficulties alluded to that have attended the use of black powder as fuse material are, chiefly, the readiness with which it takes up moisture, with consequent impairment of efficiency; its tendency to age—that is to say, to change, in the essential characteristic of rate of burning, as it continues unused; and the voluminousness of the gaseous products of its combustion. Such fuse material is contained within sheaths or envelopes of considerable strength; and, under such conditions of confinement, the gases generated in the burning of the fuse bring about pressure conditions at the point of burning such as to accelerate combustion, and so to alter the rate of burning.

Substitutes have been proposed—thermite, nitrocellulose compositions, and others. These all lack one characteristic that black powder possesses, and it is a characteristic of great practical value. A fuse of black powder, when it burns to the end, gives an "end spit"—it projects a spurt of flame and incandescent particles upon the adjacent body to be fired. It is by virtue of this characteristic that black powder has continued in the field, not successfully displaced as a fuse material.

Black powder is, typically, a composition of sodium or potassium nitrate, charcoal, and sulphur; and it is mainly by varying the ratio of the ingredients that the rate of burning for safety-fuse and time-fuse services is varied. It is not difficult to produce a composition of fast rate of burning—a "high-speed" powder—that is relatively permanent and satisfactory; the difficulty lies in producing relatively slow burning powders. The best results in the matter of permanence are got by preparing fuse material in which are combined a fast and a slow powder. And it is the slow component in which the difficulties and drawbacks to the fullest measure of success and satisfaction are found.

Slow powder is commonly prepared by increasing the sulphur content of the composition relatively to the charcoal and the nitrate contents. Attempts have been made to reduce the rate of burning, and to produce a slow powder, not by varying the ratio in which the ingredients are compounded, but by introducing into the composition other and inert material, diluting the mass. As diluents, brick dust has been proposed, soapstone, and rosin. But these attempts have not been successful. It has been found that if added in quantities as great as 10% they render the functioning of the fuse uncertain: the continuity as a combustible body is disturbed, and the fuse is liable to burn irregularly and may go out when only partially burned. And the small permissible quantities of diluent have been found to be inadequate for the intended purpose: the rate of burning is not greatly changed. By such dilution the material, not greatly improved in the way intended, is appreciably impaired in other and unintended ways.

I have discovered that there are substances, other than those last alluded to, which, being brought to proper physical condition and added as diluents to black powder, have the desired slowing effect; and, which, even though added in large quantities, do not have prejudicial effect upon the burning. I have explored the field and have found that the diluents that I have found to be successful stand contrasted with diluents heretofore proposed (but found inadequate), not in their chemical constitution merely. I have found my successful diluents to have physical characteristics of significance not hitherto recognized.

I have been able successfully to control and lengthen the time of burning of black-powder fuses by the addition of specific substances to the powder composition. In the matter of chemical composition, I have discovered that for the purpose intended the following substances may be used with success: the oxides of tin, zirconium,

zinc, copper, titanium, iron, nickel, cobalt, manganese, and cerium; the sulphates of titanium and of barium; and the silicate of zirconium. I have used with success titanium dioxide both in undiluted condition and also that preparation of titanium dioxide precipitated upon or mingled with barium sulphate that bears in industry the name Titanox B. It sometimes is said that in the Titanox preparation the titanium dioxide is "extended" by the addition to it of the sulphate. In any case it is the titanium dioxide that is for my purposes the effective agent, and in my more generic claims I mean to include within the term "titanium dioxide" both the diluted and the undiluted material. Of all of these, I have found the compounds that afford the best results to be titanium dioxide, barium sulphate, the preparation defined of titanium dioxide and barium sulphate that is known at Titanox B, and manganese dioxide. These substances, it will be remarked, are all of them metallic compounds; they all of them, with the temperature ranges of preparation of black powder (hereinafter described) and of service are inert; they are all insoluble in water; and they all have common specific-heat characteristics, as will presently be more fully explained. These all are compounds of metals that lie in the first, second, and third long periods of groups 1, 2, 4, 7, and 8 of the periodic table of elements. Within these groups I have found no metallic compound that, being so inert, insoluble, and of proper specific heat, is inadequate to the end in view; and I believe all such compounds to be adequate.

In addition to inertness and insolubility, it will be remarked of the compounds named that all are heat stable (their melting-points exceed 800° C.); and that in every instance the specific heat is not less than 0.08 calorie per gram nor more than 0.23 calorie per gram, when measured at 0° C.

In the matter of physical condition, I have found the diluent material of my invention to be notably effective when brought to exceedingly finely divided and flake-like condition. Such condition is characteristic of the compounds named, when produced by precipitation. Such of them as may be produced otherwise will advantageously be prepared for the practice of the invention by grinding to an exceedingly fine and (ordinarily) flake-like condition.

The diluents heretofore proposed may not, for the reasons stated, be added in quantities as great as 10% by weight. I find no such practical limitation upon the addition of the materials I have named, in the enjoyment of my invention. I have found that the heavier the material employed, the larger the percentage should be, in order to achieve the result. In the case of barium sulphate, for instance, I have found an addition of 9% to be effective, substantially to reduce the rate of burning; and from that figure, in that particular instance, the percentage may range, and should range, upward (according to the degree of retardation desired) even to 50%; and this without prejudice. Obviously, in the use of any particular compound, the percentage will be varied to afford variation in, and to control, the rate of burning.

For purposes of study and comparison a standard mode of testing has been established. Lead tubes of specified size are filled with powder, and, after being filled, are closed at the ends. The tubes are then drawn through dies of specified size and reduced in diameter and elongated. Measured lengths are cut from the test pieces so prepared, the trains of powder within them ignited, and the rates of burning are noted. A powder that under such test burns at the rate of 80 seconds to the yard is a relatively fast powder. I have found that if to a powder having the rate of burning of 80 seconds to the yard I add specific metallic oxides in the ratio of 30%, I reduce the rate of burning to the following figures:

Using 30% titanium dioxide, rate of burning reduced to 160–200 sec./yd.

Using 30% manganese dioxide, rate of burning reduced to 115–150 sec./yd.

Using 30% copper oxide, rate of burning reduced to 105–140 sec./yd.

Using 30% zirconium oxide, rate of burning reduced to 105–140 sec./yd.

It has already been remarked that the relatively fast burning powders are the more stable, and, accordingly, it is better to practise the invention upon powders that otherwise are of fast-burning composition; a like retarding effect, however, may be gained in the case of powders that otherwise are of a relatively slow-burning composition. For example, by combining with a 120 sec./yd. powder a 30% addition of titanium dioxide the rate of burning may be reduced to 260 sec./yd.; and, by the same addition, a 200 sec./yd. powder may be reduced to a 300 sec./yd. powder.

The 30% addition is named by way of illustration. As I have said, the addition being greater or less, the degree of retardation so effected will be greater or less. And it will further be understood that by making choice between specific compounds and by combining specific compounds, variation in the intensity of the slowing effect may be gained.

Suitable methods of procedure are (1) to introduce the slowing agent into the wheel mill used in the production of black powder, along with the charcoal, the sulphur, and the alkali-metal nitrate, and to mix the whole at once; (2) to introduce the slowing agent into the mill after the charcoal, the sulphur, and the alkali-metal nitrate have been mixed and brought to the condition of a cake, and to effect the incorporation of the slowing agent into the cake by continued mill operation; and (3) to add the slowing agent to the charcoal and the sulphur while in a ball mill, prior to the wheel-milling operation. In any case the slowing agent is incorporated while the powder is in course of preparation, regardless of whether it is to be a simple contact mixture or an incorporation by a milling process; for after that the slowing agent may not be so effectively introduced.

The addition to black powder of any of the substances that I have specified has the effect of lowering the powder's total heat of reaction, its burning temperature, and its rate of burning. The specific heats of various added materials (primarily substances of my invention; but with them, for purposes of comparison, other substances also), as well as of the component materials of black powder, are given in the ensuing Table No. 1. From these heats, the specific heats of the slow powders have been calculated and are given in Table No. 2, along with the burning times of the same powders in lead tubes. It will be noted that the burning times of a number of these powders increase with the specific heat of the powder. Therefore, it appears that there is a trend towards slower burning with the increased specific heat of the powder, which in turn is caused by the high specific heats of the added materials.

TABLE No. 1

Specific heats of substances taking part in the burning reactions of slow powders and black powders

Substance	Specific heat cal./gm.
Black powder materials	
Potassium nitrate	0.214
Sulphur	0.176
Charcoal	0.160
Slow powder added materials	
Tin oxide	0.090
Zirconium oxide	0.103
Barium sulphate	0.111
Zinc oxide	0.114
Copper oxide	0.125
Titanox-B	0.135
Iron oxide	0.148
Manganese dioxide	0.152
Titanium dioxide	0.168
Calcium carbonate	0.203
Magnesium silicate	0.275

TABLE No. 2

Effect of specific heats of powders on their burning times in lead tubes

Sample No.	Powder composition		Specific heat of powder	Burning time of powder (sec./3 ft.)
	Black powder	Added material		
	Percent	*Percent*		
1	100		0.201	84
2	71.4	Tin oxide—28.6	.170	91
3	71.4	Zirconium oxide—28.6	.174	108
4	71.4	Barium sulphate—28.6	.176	176
5	71.4	Zinc oxide—28.6	.177	100
6	71.4	Copper oxide—28.6	.180	104
7	71.4	Titanox-B—28.6	.183	150
8	71.4	Iron oxide—28.6	.186	118
9	71.4	Manganese dioxide—28.6.	.188	129
10	71.4	Titanium dioxide—28.6.	.192	161
11	71.4	Calcium carbonate—28.6.	.202	234
12	71.4	Magnesium silicate—28.6.	.223	242

Of the substances of these tabulations, all but two prove themselves to be useful for the end in view. Calcium carbonate is water decomposable and magnesium silicate carries a large content of water of crystallization; and for such reasons alone these compounds would be inadequate; however, the fuses in which they were compounded, in course of burning, went out. This inadequacy I ascribe to their high specific heats. The specific heat of an added material may be too high, as well as too low, to afford the desired slowing effect and at the same time not to interfere nor prevent the sure functioning of the fuse.

The results tabulated would seem not fully to substantiate the principle that the greater the specific heat of the material chosen, the more pronounced the slowing effect. This seeming aberration is, however, explicable. There is another concomitant principle; namely, that the finer the degree of subdivision to which the adulterant material is reduced, the more pronounced will be the slowing effect. The tabulation gives the practical results, when these two principles are in operation and in accommodation to one another. Specifically (and with reference to Table No. 2), the slow powders containing barium sulphate, zirconium oxide, and Titanox B produce more slowing than their specific heats alone would warrant, because of their extremely small particles and the shape of these particles.

The reason why the smaller and flatter-shaped particles produce greater slowing than large or spherical-shaped particles of a material may be explained by considering the steps that take place in the burning of the powder. The slow powder consists of black powder and inert material in intimate mechanical mixture. Thus the particles of the components or of the mixed black powder become coated with the inert material, and the finer flatter particles provide the better coatings. When this slow powder is heated, the sulphur will not melt quite so readily (although the ignition temperature is not increased); the nitrate does not decompose so readily; and the oxygen molecules cannot attack the carbon as easily, because the inert material provides a barrier to the progress of the oxygen molecules to the carbon surface—i. e., the mean free path of the molecules is changed. Also the small, flat particles present a greater specific surface than large, spherical-shaped particles; which tends to absorb the heat of reaction more rapidly, and consequently slows the combustion. Since the rate of burning of the fuse is dependent upon the combustion of the powder, the burning rate will also be slowed up.

Thus it appears that the slowing action of the added materials in the slow powders is caused by three factors, viz, (1) their specific heats, (2) their particle size, and (3) their particle shape.

The burning temperatures of the slow powders of this invention are lower than that of the black powder from which they are produced. The reason for this is that the slow powders always contain less combustible material than the undiluted black powders; they, therefore, produce less heat from the same mass. Since temperature is the ratio of heat to mass, the slow powders have lower burning temperatures. Accordingly, they cause less charring of the fuse structure, and less gas is evolved from the burned fuse materials. The powders of the invention produce less gas when burned in lead tubes, both because the burning temperatures are less and because there is less combustible material per unit of mass than is the case with ordinary black powder.

The powder of my invention takes up moisture less readily than does unmodified black powder; its deterioration with age is less; and the burning pressures, built up by generated gases, are less.

Within the term "black powder" I means to include powders compounded of sulphur, carbon, and alkali-metal nitrate. And, furthermore, the alkali-metal nitrate being replaceable by other nitrate or oxidizing agent, I intend to bring such substitutions also within the field of enjoyment of my invention.

In a companion application, Serial No. 100,383, filed September 11, 1936, I claim a slow-burning powder composition consisting of black powder modified by the addition of barium sulphate or lead sulphate.

I claim as my invention:

1. A slow-burning powder composition, consisting of black powder modified by the addition of titanium dioxide.

2. A slow-burning powder composition, consisting of black powder modified by the addition of a precipitation of titanium dioxide upon barium sulphate.

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