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DELAY COMPOSITION

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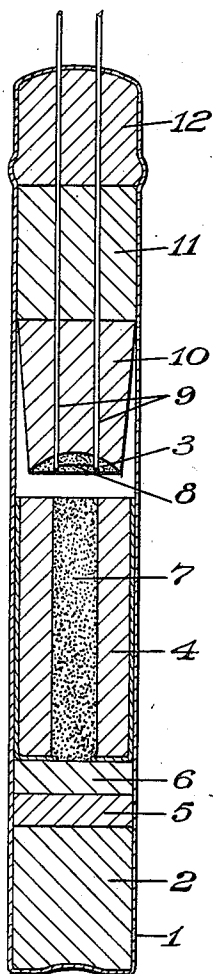


Fig. 1

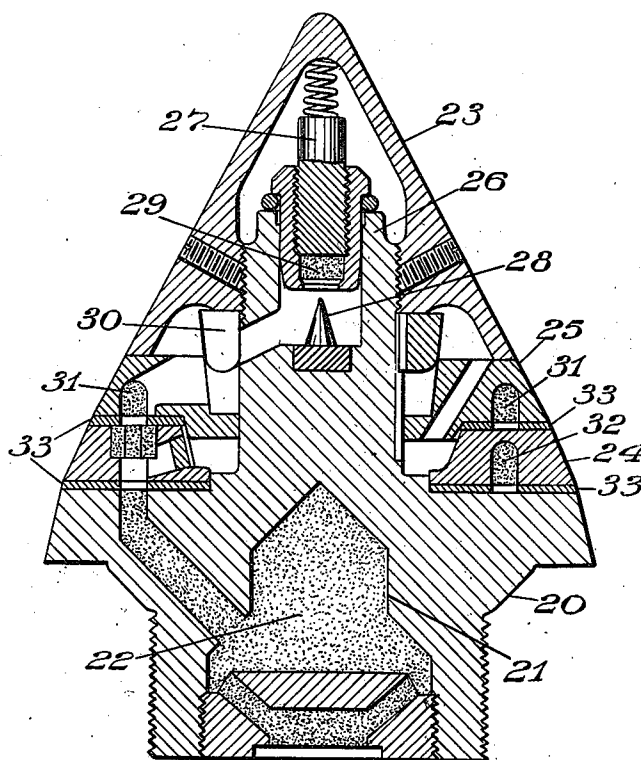


Fig. 2

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DELAY COMPOSITION

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The present invention relates to a new and improved burning composition, and more particularly to a composition particularly suitable for use as a delay element or time fuse in delay detonators.

Delay detonators may be conveniently classified into two main types, depending on the purpose for which they are employed. The first type, represented by the delay electric blasting cap, is employed in ordinary commercial blasting operations. The second type, represented by the fuse head of military shells is employed especially in high explosive shells which burst in air, or in a calculated length of time after impact.

Although the purpose for which these delay detonators are employed is entirely different, in construction they are essentially alike. Both types consist essentially of a detonating base charge separated from an appropriate firing means by a suitable length or column of a slow-burning ignition composition. In the fuse head the firing means generally comprises a percussion composition which is initiated by impact. In delay blasting caps, the firing means commonly consists of a high resistance electric wire surrounded by a highly inflammable ignition composition which bursts into flame when an electric current heats the wire to incandescence. The percussion or ignition composition as the case may be, ignites the fuse or delay element which burns slowly. Eventually, after a definite interval of time, this initiates either a more violent ignition agent, a priming composition or a detonating base charge.

The slow-burning fuse or delay compositions above referred to have heretofore generally been of the gas-generating type. Thus, for example, modified black powder compositions which evolve a great amount of gaseous combustion products, have been extensively employed in both types of delay detonators. Such compositions, however, are highly undesirable both in the military and the commercial type of delay detonator because a vent must be provided for the escape of these gases. In fuse heads, this is objectionable because the rate of combustion varies with the pressure, and therefore the time interval of the delay will vary with the altitude of the shell during flight. In delay blasting caps, on the other hand, the escape of the hot gaseous combustion products is objectionable because premature detonation of the main explosive charge with which the detonator is employed is apt to result. In addition, the vent provides a means of

ingress of moisture or other harmful substances as well as a means of efflux of the gaseous ignition products. For these and other reasons, substantially gasless delay compositions are highly desirable for use in delay detonators.

Relatively few delay compositions have been proposed heretofore, and all of these appear to possess certain disadvantages which detract from their otherwise desirable properties. Thus, the composition disclosed by Eschbach in GB 371,596, consisting of antimony and potassium permanganate is not altogether satisfactory for several reasons. In the first place the composition, as disclosed, is difficult to ignite, for which reason it is not altogether reliable in a delay detonator. In addition, the composition burns rather rapidly, for which reason a very long fuse or delay train must be employed to produce a ten-second delay, for example. Lastly, the composition is difficult to standardize so that a given length of delay element will burn within a given length of time.

The selenium-barium peroxide composition disclosed by Nash in U. S. Patent No. 1,960,591 also has certain disadvantages. This composition likewise burns rapidly. In addition the ingredients are not readily available, and the selenium required is unpleasant to work with because of its physiological effects.

The object of the present invention is a new and improved delay composition. A further object is a substantially gasless delay composition which is readily ignited and reliable in use. A still further object is a composition of the character described which has a slow, uniform rate of combustion and which produces substantially no gaseous ignition products. Other objects will be apparent as the invention is more fully described hereinafter.

We have found that these and other objects may be accomplished by means of the following invention whereby the burning speed of a delay composition comprising a metal and an oxidizing agent may be varied within wide limits.

We have found that the burning speed of ignition compositions comprising an oxidizing agent and a given metallic element A may be altered within wide limits by alloying said element A with another metallic element B which has a heat of combustion per unit volume appreciably different from the corresponding thermochemical property of the given metal A. In order to accelerate the burning speed of the composition, the metallic element A is alloyed with a metal B whose heat of combustion per unit volume is greater than the corresponding property of the

element A. In order to retard the burning speed of the composition, the given metallic element A is alloyed with a metal B whose heat of combustion per unit volume is less than that of the given element A. The above mentioned thermochemical property, which will hereinafter be referred to as the "thermochemical constant K" for the given metallic element, is obtained according to the following equation:

$$K_A = \frac{H_{AO}}{(x)M_A \times d_A}$$

where K_A is the thermochemical constant of the metallic element A. H_{AO} is the heat of formation of the oxide of the metal A in gram-calories; M_A is the molecular weight of the metal A and d_A is the density of said metal A. x is the number of atoms of element A in the oxide for which the heat of formation is taken.

In order to describe our invention more clearly, reference is made to the accompanying table showing several compositions which demonstrate the control which may be exercised over the burning speed of a given ignition composition by the proper selection of the element B to be alloyed with the reference metal A. It is to be understood, however, that this is done solely by way of illustration, and is not to be construed as a limitation upon the scope of our invention, which has many important applications other than those particularly described hereinafter.

Referring generally to the table, Examples 1 and 2 represent suitable reference compositions in which the metal A is not alloyed with any other element. Example 3 illustrates the accelerating effect of alloying A and B, where K_B is greater than K_A . Examples 4-9 illustrate the retarding effect of alloying A with B where K_B is less than K_A . For the purpose of illustrating the relative effects of alloying a given element A with various other elements, Examples 3 and 5-9 relate to delay compositions comprising antimony, while Example 4 illustrates the application of our invention to other elements than antimony. Examples 7 and 9 illustrate the effect of the amount of retarding element B on the burning speed of the composition.

respectively) the burning speeds of the compositions comprising these respective alloys will be less than that of a similar composition in which antimony is the only metal present. In the case of the antimony-copper alloy, this effect is accomplished by the use of only two parts of the latter element with 98 parts of antimony, a greater per cent of copper serving to retard the speed still further, as seen in Example 9.

The converse effect is illustrated by Example 3, where antimony is alloyed with iron. Since K_{Fe} is greater than K_{Sb} , the burning speed of the composition comprising the alloy is faster than that of the corresponding composition in which antimony is the only metal.

This peculiar effect of retarding or accelerating the burning speed of a given composition is not brought about to a controlled extent by mechanical mixtures of the two metallic elements with an oxidizing agent, but the advantageous effect is dependent upon the fact that the two metals are alloyed together. Thus, for example, a mechanical mixture of copper, antimony and permanganate is very difficult to ignite and once ignited invariably burns out. On the other hand, a composition comprising these same ingredients, in the same proportion, will ignite readily and burn regularly and smoothly without producing any substantial amount of gas, if the copper is alloyed with the antimony.

In order to describe the application of our invention, we shall refer to the accompanying diagrams which illustrate two embodiments thereof. This is done solely by way of illustrating the utility of our invention, and is therefore not to be regarded as a limitation upon the scope thereof.

Referring to the diagrams, Figure 1 represents a sectional elevation of a delay electric blasting cap in accordance with our invention, while Figure 2 represents a similar view of a military fuse head for an explosive shell, provided with a time ring fuse.

Referring particularly to Figure 1, the detonator comprises a base charge 1 in a ventless shell 2, said base charge being separated from the ignition composition 3 by the metal delay element

Table

50	Example	Metal used				Composition of Ignition mixture		Burning speed: sec./in. when composition is loaded in metal tube	K		Effect of B on burning speed
		Elements present		Composi- tion							
		A	B	Per- cent A	Per- cent B	Part metal	Parts KMnO ₄		K _A	K _B	
60	1.-----	Sb		100	-----	2	3	8.6	102.5	-----	Standard.
	2.-----	Al		100	-----	1	2	2.2	2680	-----	Do.
	3.-----	Sb	Fe	50	50	1	1	3.68	102.5	224	Accelerate.
	4.-----	Al	Mn	60	40	1	2	5.1	2680	307.5	Retard.
	5.-----	Sb	Bi	50	50	1	1.13	10.9	102.5	35.6	Do.
	6.-----	Sb	Cd	75	25	1	1.22	9.1	102.5	68.2	Do.
	7.-----	Sb	Cu	98	2	2	3	10.5	102.5	65.8	Do.
	8.-----	Sb	Pb	75	25	1	1.14	11.9	102.5	21.6	Do.
	9.-----	Sb	Cu	92.5	7.5	2	3	13.2	102.5	65.8	Do.

From the foregoing table, it will be seen that where a given metallic element A is alloyed with another metallic element B, the burning speed of the composition comprising the resulting alloy will be greater than the burning speed of the composition comprising the unalloyed element A if K_B is greater than K_A . Conversely the burning speed will be slower, if K_B is less than K_A . Thus, by alloying antimony with bismuth, cadmium, copper or lead (Examples 5, 6, 7, 8 and 9

4, the ignition composition 5, and the priming composition 6. The metal delay element 4 is tightly packed with a slow burning substantially gasless composition 7 comprising 1.1 parts of potassium permanganate and one part of an alloy consisting of equal parts by weight of antimony and bismuth. The ignition composition 3 surrounds the high resistance bridge wire 8 between the two leg wires 9. The leg wires are held in fixed space relationship by the bridge

plug 10. The upper end of the shell 2 is closed by means of a waterproofing composition 11 and a sulfur seal 12.

The interval of time between the instant of firing the cap and the instant of detonation will, of course, depend on the length of the delay element 4. For example, a delay element may be used in the manner above described, having a delay of 15.4 seconds, which is obtained with a maximum variation of 0.35 second. Since this maximum variation is considerably less than the interval between successive delays, no overlapping of the delays will be observed.

Referring now to Figure 2, the body of the fuse 20 is of conventional design and construction. Within the chamber 21 of the body 20, the usual magazine charge 22 is placed. The closing cap 23 is of any desired construction except that the usual venting aperture is omitted. The time train rings 24 and 25 are of usual construction and are clamped in position against the body 20 by the closing cap 23, which engages the threads on the extension 26 of the body 20. Washers 33 are provided so that the engagement is water-tight. The extension 26 is drilled out at the upper end to form a plunger-chamber for the plunger 27 and the firing pin 28, which is adapted to strike the percussion composition 29 in the end of the plunger 27.

When the firing pin 28 strikes the percussion composition 29, the flame is communicated through the passage 30 of the powder train 31, carried by the time train ring 25. The powder train 31 in turn ignites the powder train 32 in the time train ring 24, the point of ignition being determined by the relative adjustment of the time train rings with respect to each other. The magazine charge 22 is fired by the powder train 32, and the former in turn fires the explosive charge contained in the shell proper.

The powder trains above referred to (31 and 32) may comprise any of the delay compositions in accordance with our invention. Preferably, however, the composition consists of 1.1 parts of potassium permanganate and 1 part of an alloy consisting of 50% antimony and 50% bismuth. Such a powder train burns with a slow, even speed, is readily ignited, and is not apt to burn out. Substantially no gas is evolved hence the rate of burning of the composition will not be appreciably affected by changes in pressure during the course of the shell's flight.

In the foregoing description of our invention we have cited, by way of example, several compositions comprising an alloy and potassium permanganate. It is apparent that other oxidizing agents may be used in the same manner. Thus, for example, we may employ potassium chlorate or perchlorate, sodium dichromate, calcium peroxide, barium peroxide and the like as oxidizing agent. Permanganate is to be preferred, however, since the composition burns more regularly, and the products of combustion are substantially gasless under the conditions obtaining.

It is also apparent in the above description that other metals than those specifically cited may be alloyed with antimony in accordance with our invention. The effect upon the burning speed produced by alloying any particular metal with antimony may be readily ascertained by comparing the thermochemical constant K of the particular metal with that of antimony, as hereinbefore explained.

While we have illustrated our invention with particular reference to antimony alloys, it is

apparent from the foregoing description that the retarding or accelerating effects produced by alloying any element B with any other element A may be predicted on the basis of the disclosed principle. This may be conveniently accomplished by arranging a series comprising any desired number of metallic elements in the order of increasing value of the thermochemical constant K. In this series the effect of alloying any element A with any other element B may then be readily determined from the relative positions of the respective elements in the series. If B is above A in the series, the burning speed of the ignition composition comprising the alloy A—B will be greater than that of the composition comprising the unalloyed element A. The converse will be true if B is below A in the series.

As illustrative of this application of our invention, we may list the given metals, aluminum, antimony, bismuth, cadmium, copper, iron, lead, magnesium and manganese in the order of increasing values of K as in the following table. It will be understood that the heats of combustion of the different metals will be dependent on the degree of oxidation of the metal, where the formation of more than one oxide is possible. This in turn will be influenced by the oxygen balance of the composition. The oxide used as the means of calculation is designated in the table below.

Metal	Oxide	K
Pb.....	PbO.....	22.2
Bi.....	Bi ₂ O ₃	33.6
Cu.....	CuO.....	60.9
Cd.....	CdO.....	67.1
Sb.....	Sb ₂ O ₃	103.5
Fe.....	Fe ₂ O ₃	228.0
Mn.....	Mn ₂ O ₃	235.7
Al.....	Al ₂ O ₃	2600
Mg.....	MgO.....	3490

In this series for example, a composition comprising Fe alloyed with Sb, Cd, Cu, Bi or Pb will have a slower burning speed than a similar composition comprising Fe alloyed with Mn, Al or Mg. Many other applications of our invention will be apparent to those skilled in the art. The method presupposes a proper control of oxygen balance in the preparation of delay compositions, by suitable proportioning of oxidizing agent and alloy.

In the foregoing detailed description of our invention, we have illustrated its application to delay electric blasting caps and to time ring fuses. It is apparent, however, that our invention has many important applications besides those herein particularly described with reference to the diagrams. It is also apparent that many variations in detail may be made without departing from the spirit and scope of our invention. We therefore intend to be limited only in accordance with the following patent claims:

We claim:

1. A delay detonator wherein the delay element is charged with a delay composition of predetermined burning speed consisting of an oxidizing agent and a metal component comprising an alloy of antimony with at least one metal whose heat of combustion per unit volume is substantially different from that of antimony.

2. A delay detonator wherein the delay element is charged with a delay composition of predetermined burning speed consisting of an oxidizing agent and a metal component comprising an alloy of antimony with at least one metal

whose heat of combustion per unit volume is greater than that of antimony.

3. The delay detonator of claim 2 wherein the metal alloy of antimony comprises iron.

5 4. A delay detonator wherein the delay element is charged with a delay composition of predetermined burning speed consisting of an oxidizing agent and a metal component comprising an alloy of antimony with at least one metal
10 whose heat of combustion per unit volume is substantially less than that of antimony.

5. The delay detonator of claim 4 wherein the metal alloy with antimony is selected from the group consisting of bismuth, copper, cadmium
15 and lead.

6. A delay detonator wherein the delay element is charged with a delay composition of predetermined burning speed consisting of non-explosive ingredients including an oxidizing

agent and an alloy of antimony with at least one metal whose heat of combustion per unit volume is substantially different from that of antimony.

7. A delay detonator wherein the delay element is charged with a delay composition of predetermined burning speed consisting of non-explosive ingredients including an oxidizing agent and an alloy of antimony with at least one metal whose heat of combustion per unit volume
5 is greater than that of antimony.

8. A delay detonator wherein the delay element is charged with a delay composition of predetermined burning speed consisting of non-explosive ingredients including an oxidizing agent and an alloy of antimony with at least one metal whose heat of combustion per unit volume
10 is substantially less than that of antimony.

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