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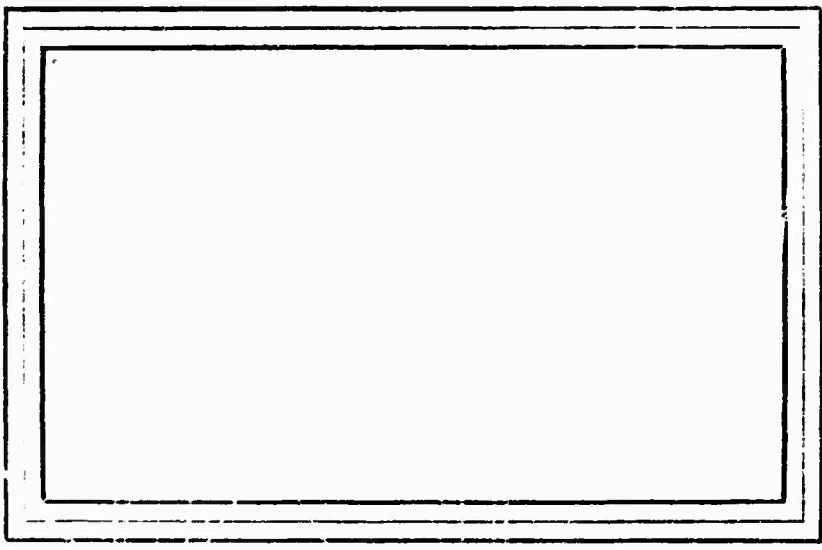
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U. S. NAVAL AMMUNITION DEPOT
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IGNITION THEORY:
APPLICATION TO THE DESIGN
OF NEW IGNITION SYSTEMS

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ABSTRACT

A theory is presented on the ignition of solid compositions. The effect of certain physical, chemical and thermal properties of a solid composition on the ignition time and ignition energy is explained and supported by experimental evidence.

Different types of ignition systems are described. Problem areas of the normal ignition systems are discussed and a technique to overcome these problem areas is offered.

By use of the developed ignition theory and a hot-bath immersion test apparatus, a technique of determining the true ignition temperature of a composition is described.

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1. Background and Purpose.

a. The design and development of new and/or improved ignition systems for pyrotechnic compositions have been hindered to a large degree due to the lack of knowledge of, or the insight into, the important parameters involved in the ignition of pyrotechnic compositions.

b. With a basic understanding of the theory of ignition of solid compositions, the conception of new ignition systems should be greatly aided.

c. It is the purpose of this report to provide a theory of ignition that will offer this basic understanding. The theory will demonstrate the magnitude of importance of the various physical and chemical properties involved in the ignition of a solid composition.

d. A means of determining a true ignition temperature for compositions will also be presented.

2. Physical Model.

a. Composition Description.

(1) The composition will be defined as a solid material that, when heated to a given temperature, will ignite and combust without further heating by an external source. This temperature will be defined as the ignition temperature, T_s .

b. Heat source.

(1) For this model, a heat source of constant heat flow, q_{in} , will be assumed.

(2) The physical type of heat source, i.e., radiant,

hot gas, hot wire, etc., will not be described.

c. Heat transfer.

(1) The mode of heat transfer through the composition will be assumed to be a one dimensional, conductive process with the thermal conductivity of the composition being independent of temperature.

3. Development of Ignition Theory.

a. Ignition time.

(1) By definition, the ignition time, t , will be the time required to raise the temperature of the surface of the composition from some ambient temperature, T_a , to the ignition temperature, T_s , with a constant rate of heat input, q_{in} , into the composition.

(2) Integration of the basic heat equation

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} \quad \text{EQ. (1)}$$

yields

$$\frac{T - T_s}{T_a - T_s} = \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{\sqrt{4\alpha t}}} e^{-z^2} dz \quad \text{EQ. (2)}$$

which yields, when integrated,

$$\frac{\partial T}{\partial x} = \frac{(T_a - T_s)}{\sqrt{\pi\alpha t}} e^{-\frac{x^2}{4\alpha t}} \quad \text{EQ. (3)}$$

where $t > 0$ and $0 < x < L$ and

where L is the length of the composition.

From the one-dimensional heat flow equation

$$q_{in} = -KA \frac{\partial T}{\partial x} = \frac{\partial H}{\partial t} \quad \text{EQ. (4)}$$

substitution for the temperature gradient, $\frac{\partial T}{\partial x}$, from

Equation (3), produces

$$q_{in} = \frac{KA(T_s - T_a)}{\sqrt{\pi\alpha t}} e^{-\frac{x^2}{4\alpha t}} \quad \text{EQ. (5)}$$

Defining the specific heat of the composition, C, as

$$C = -\frac{1}{m} \cdot \frac{\partial H}{\partial T} \quad \text{EQ. (6)}$$

and the mass, m, as

$$m = \rho A x \quad \text{EQ. (7)}$$

appropriate substitutions into Equation (4) yields

$$\frac{\partial x}{\partial t} = \frac{k}{\rho c x} = \frac{\alpha}{x} \quad \text{EQ. (8)}$$

If Equation (8) is integrated between the limits of X_0 to X and t_0 to t, where $X \gg X_0$ and $t \gg t_0$, then, an equation, Equation (9), is available which, for practical purposes, is correct, except when x or t approaches zero.

$$x^2 \cong 2 \alpha t \quad \text{EQ. (9)}$$

Substitution from Equation (9) for x^2 into the exponential term in Equation (5) yields Equation (10).

$$q_{in} = \frac{KA(T_s - T_a)}{\sqrt{\pi e \alpha t}} \quad \text{EQ. (10)}$$

From this expression, it is possible to solve for the ignition time, t, for a constant rate of heat flow, q_{in} , into the composition which ignites at the ignition temperature, T_s .

The expression for ignition time is shown in Equation (11).

$$t = \frac{K^2 A^2 (T_s - T_a)^2}{\pi e \alpha q_{in}^2} \quad \text{EQ. (11)}$$

Knowing that the thermal diffusivity, α , is equal to $\frac{k}{\rho c}$, yields another expression for the ignition time, as illustrated by Equation (12).

$$t = \frac{K \rho c A^2 (T_s - T_a)^2}{\pi e q_{in}^2} \quad \text{EQ. (12)}$$

b. Ignition energy requirements.

If the ignition energy, E , of a system is defined as

$$E = q_{in} t \quad \text{EQ. (13)}$$

and this expression is substituted into Equation (12), it is apparent that the ignition energy requirements is a function of two variables, the ambient temperature, T_a , and the rate of heat flow, q_{in} , into the composition.

$$E = \frac{K \rho c A^2 (T_s - T_a)^2}{\pi e q_{in}} \quad \text{EQ. (14)}$$

4. Experimental Verification of the Developed Ignition Theory.a. Ignition by radiant fluxes and hot gases.

(1) From data of Baer and Ryan¹ and Keller, Baer and Ryan², it is evident that Equation (12) is supported and verified for both radiant flux and hot gas sources.

(2) Various rates of heat flows or fluxes were used and it was observed that the product, $q_{in}^2 t$, was essentially a constant, as would be predicted by Equation (12).

b. Ignition temperature.

(1) From the previously mentioned data^{1,2}, the results of experiments indicate that the ignition temperature is probably a constant value. This could not readily be verified, since the assumption of a constant thermal conductivity introduced an uncertainty as to whether the ignition temperature, T_s , changed or the thermal conductivity, K , changed during the course of experimental variances. The ignition temperatures calculated from the referenced experimental work had a range of 59°C, thus it is difficult to assess the assumption of a

constant ignition temperature from this work.

(2) However, from experimental results presented later in this report, the assumption of a constant ignition temperature for a given composition is rather strongly supported. In this case, a range of only 10°C was observed.

c. Ambient temperature effect. The effect of ambient temperature upon the ignition time as predicted by Equation (12) is supported by experimental data ^{1,2}. Ambient temperature effects were evaluated from $+60^{\circ}$ Centigrade to -60° Centigrade, and the ignition time was found to obey the general equation form as depicted by Equation (12).

d. Ignition energy requirements. Obviously, from the verification indicated upto this point, the ignition energy requirement, E , as defined by Equation (14), is also supported.

5. Consequences of the Ignition Theory.

a. Prime ignition sources.

(1) The prime ignition source in pyrotechnic items is normally an impact-sensitive primer or an electrically-fired squib. Both types of these prime ignition sources produce relatively high rates of heat flow for very short periods of time.

(2) Due to the short times involved, it is necessary that the ignition composition to be ignited has as low an energy requirement as possible, since the time interval that the source is producing heat flow is generally less than 250 milliseconds.

b. Ignition composition requirements.

(1) The ignition composition, sometimes referred to as a transfer mix or first-fire composition, serves two main purposes. It must be sensitive enough to ignite upon contact with the heat flow from the prime ignition source and also provide a means of igniting the main pyrotechnic composition after its own ignition and combustion have occurred.

(2) Physical and thermal properties of the ignition composition is very important. To hold the ignition energy requirements to a minimum, it is obvious, from studying Equation (14), that it is desirable to maintain as low thermal conductivity, density and specific heat values as possible.

(3) Likewise, the area to which the heat flow from the prime ignition source is directed is very important. By directing the flow of hot gases from the prime ignition source to smaller areas of the ignition composition, the ignition energy requirements can be greatly reduced, thus increasing the probability of ignition under adverse conditions.

c. The design of normal types of ignition systems.

(1) Loose or powdered ignition composition.

(a) One of the normal ignition systems used in the ignition of red phosphorus-containing smoke compositions is the loose or powdered ignition composition system.

(b) In this system, the powdered or granulated ignition composition is simply poured on to the surface of the red phosphorus smoke composition and an electric squib

is fired directly into the ignition composition.

(c) As might be expected, the burning time of the loose composition is rather short, and all of the energy released by the ignition composition is not adsorbed by the red phosphorus composition.

(d) Some of the inherent problems of this type of system can be illustrated by use of Equations (12) and (14). For example, in the case of the red phosphorus composition, an ignition temperature of approximately 550° Centigrade is observed. If the ignition times for ambient temperatures of 30° Centigrade and -50° Centigrade are considered, it becomes obvious that the ratio of the expected ignition times would be as shown by Equation (15).

$$\frac{t_{30}}{t_{-50}} = \frac{(550 - 30)^2}{(550 + 60)^2} = 0.73 \quad \text{EQ. (15)}$$

(e) This ambient temperature effect would predict that only 73% of the energy required at -50°C is required at 30°C.

(f) However, this is not the sole effect of a lower ambient temperature. Further examination reveals that the rate of heat flow into the composition would be reduced due to the slower combustion rate of the ignition composition at -50°C as compared to +30°C. If q_{in} was decreased to one-half its initial value, Equation (12) would predict that the ignition time would be increased by a factor of four. When this effect and the direct ambient temperature effect is

considered, it is seen that the ignition time would be increased by a factor of 5.5, approximately.

(g) Thus, if this possibility was not considered initially in the design of the ignition system, it is easily seen how some ignition failures could result at low ambient temperatures.

(2) Consolidated ignition composition systems.

(a) Another general type of ignition system used in pyrotechnics consists of an increment of ignition composition pressed directly on top of the main pyrotechnic. This technique is normally used on flare compositions and, sometimes, on red phosphorus compositions.

(b) Normally, this ignition composition is sensitive to ignition from the primary heat source and combusts at a rate much slower than the powdered or loose ignition composition system.

(c) The primary means of ignition of the main pyrotechnic composition are accomplished by the conduction of heat from the flame front of the ignition composition back into the unburned ignition composition and into the main pyrotechnic composition. When a sufficient amount of heat has been transferred to the main pyrotechnic composition such that the ignition temperature is reached, combustion of the main pyrotechnic ingredient proceeds.

(d) If the ignition composition does not produce a sufficient rate of heat flow back into the main pyrotechnic

composition, ignition will not occur. This has been observed when illuminant flare composition was used as the ignition composition on red phosphorus composition at an ambient temperature of -65°F .

(e) From the one-dimensional heat flow equation (Equation 4), it is obvious that a high temperature gradient would be desirable in order to obtain high rates of heat flow back into the composition. This suggests strongly that high reaction temperatures are necessary in the ignition composition when the main pyrotechnic composition has a large ignition energy requirement.

d. The design of improved ignition systems.

(1) Some problem areas have been pointed out in the normal types of ignition systems. These problem areas are directly related to the effects of ambient temperature upon the ignition energy requirements of both the ignition and main pyrotechnic compositions and on the rate of heat flow into these compositions.

(2) Since it is impossible to remove these effects, it is necessary to design around these effects.

(3) One of the most critical changes that occur with ambient temperature is that of the change in the rate of heat flow, q_{in} , into the composition. If this change in the rate of heat flow could be minimized, most of the effect of ambient temperature on the ignition system would be negated.

(4) This can be achieved rather easily by using an

ignition composition that produces a heat source that is basically a radiant energy source. For example, a pyrotechnic mixture containing roughly 60% magnesium and 40% sodium nitrate will produce a maximum reaction temperature which is fairly constant for normal variations in ambient temperature. If the flame of this composition is allowed to come in contact with the surface of the main pyrotechnic composition to be ignited, an extremely high rate of heat flow into the composition is available, which is essentially independent of ambient temperature.

(5) The manner in which the flame is introduced to the main pyrotechnic composition leaves much leeway from a design standpoint.

(6) Depending on the availability of space in the hardware and weight requirements, several designs are especially adaptable to the normal pyrotechnic items where cigarette-fashion burning is predominant.

(7) The use of hollow-center, cylindrical ignition composition pellets has been found to be very successful in the ignition of red phosphorus composition at -65°F . The hollow center allows the high temperatures of the flame from the pellet to impinge directly on the surface of the red phosphorus composition for several seconds, which are more than needed, even at -65°F .

(8) Another method is to recess a flare-type pellet into the main pyrotechnic composition such that while the

pellet is burning, the high temperature flare is impinging on the top of the main composition and, to a fair degree, inside the main composition.

(9) The advantages of using these techniques or similar techniques where a flare-type composition is used as the ignition energy source becomes obvious when available energy is considered. Flare compositions release about three to four times as much energy as the normal ignition mixes used in most pyrotechnics, when compared on a weight basis.

(10) The normal ignition mix consists of a fuel, which is usually silicon, zirconium, aluminum, titanium, manganese or boron, and an oxidizer, which is usually iron oxides, lead dioxide, red lead dioxide, barium peroxide, cuprous oxide, barium chromate or lead chromate. None of these combinations of fuel and oxidizers will produce the large heat of reaction that flare compositions typically produce.

6. Ignition Temperature Determination.

a. Normal methods of the determination of ignition temperatures.

(1) Three methods commonly used in the determination of ignition temperatures are differential thermal analysis (DTA), thermal gravimetric analysis (TGA) and the hot-bath immersion technique.

(2) The results of all three techniques are subject to the rate at which heat is applied to the sample. The

indicated ignition temperatures of a given sample by DTA or TGA techniques will vary depending on the rate of temperature rise of the sample or the heating rate. Likewise, the hot-bath immersion technique affords similar problems in that the time for a given sample to ignite is a function of the bath temperature, sample weight and the test apparatus.

(3) Because of these problems, it is extremely difficult to assign a value to the ignition temperature of a given material.

b. Suggested means of determining a true ignition temperature.

(1) Using a hot-bath immersion test apparatus, a novel technique is available that allows the determination of a true ignition temperature. This test apparatus usually consists of a thin-walled metallic sample cup and a liquid hot-bath of molten lead or Wood's metal. After placing the sample composition in the cup, the cup is immersed in the bath and the time lapse between immersion of the sample cup and the ignition is recorded for the particular bath temperature used.

(2) A typical set of ignition times and bath temperatures for the ignition of a 10% boron - 90% barium chromate is listed below:

<u>Bath Temperature, T_B</u>	<u>Time to Ignition, t</u>
702°C	25.6 seconds
682°C	35.6 "
673°C	39.4 "
659°C	73.5 "

(3) Obviously, this data does not directly indicate anything about the actual ignition temperature of the composition.

(4) However, thermal analysis of the system used for determining the time-temperature data above reveals that this information can be used to determine the true ignition temperature.

(5) Analyzing the manner in which the heat is transferred to the sample composition reveals that this system may be treated as heat flow through a composite plane wall, where the first wall encountered by the heat is a boundary layer of molten metal, of a thickness X_1 and a thermal conductivity of K_1 , and the second wall is that of the metallic sample cup, whose thickness is X_2 and thermal conductivity is K_2 .

(6) Assuming that the sample composition, when subjected to heating, acts like a material going through a phase change, i.e., the material will rise to its ignition temperature, T_s , then absorb a quantity of heat before ignition occurs, the temperature of the inside wall of the sample cup would be T_s .

(7) Knowing that the time for the cup to heat up to this temperature is in the order of 15 milliseconds, if it is aluminum as normally used, it is safe to consider this time as being insignificant to the time required to raise the sample to its ignition point.

(8) The heat flow through the first and second walls would then be that as expressed by Equations (16) and (17), respectively, and would be equal.

$$q_1 = \frac{K_1 A (T_0 - T_1)}{x_1} \quad \text{EQ. (16)}$$

$$q_2 = \frac{K_2 A (T_1 - T_s)}{x_2} \quad \text{EQ. (17)}$$

(9) If these two equations are rearranged as shown by Equations (18) and (19), and summed, Equation (20) is the result.

$$(T_0 - T_1) = \frac{q_1 x_1}{K_1 A} \quad \text{EQ. (18)}$$

$$(T_1 - T_s) = \frac{q_2 x_2}{K_2 A} \quad \text{EQ. (19)}$$

$$(T_0 - T_s) = \frac{q_1}{A} \left[\frac{x_1}{K_1} + \frac{x_2}{K_2} \right] \quad \text{EQ. (20)}$$

(10) From Equation (12), substitution of $\frac{H}{t}$ for q_{in} , where H is the heat required to ignite the sample and t is the time lapse from immersion of the sample cup to the ignition of the sample, yields Equation (21).

$$t = \frac{H^2 \pi e}{(T_s - T_a)^2 K e c A^2} \quad \text{EQ. (21)}$$

(11) Likewise, substitution of $\frac{H}{t}$ in Equation (20) for q_{in} yields Equation (22).

$$t = \frac{H}{A (T_0 - T_s)} \left[\frac{x_1}{K_1} + \frac{x_2}{K_2} \right] \quad \text{EQ. (22)}$$

(12) Combining these two equations, Equations (21) and (22), by multiplying one times the other, yields Equation (23).

$$t^2 = \frac{H^3 \pi e}{K e c A^3 (T_0 - T_s) (T_s - T_a)^2} \left[\frac{x_1}{K_1} + \frac{x_2}{K_2} \right] \quad \text{EQ. (23)}$$

(13) Thus, for a given sample weight and composition

in a hot-bath immersion test apparatus, it would be expected that the ignition time would obey this equation form. Since all factors in this equation would be constant for a given sample weight, composition and hot-bath immersion test apparatus, except the variables of ignition time, t , and the bath temperature, T_B , this equation can be expressed more simply as shown by Equation (24),

$$t^2 (T_B - T_s) = B \quad \text{EQ.(24)}$$

where
$$B = \left[\frac{H^3 \pi e}{K_e c A^3 (T_s - T_a)^2} \right] \left[\frac{X_1}{K_1} + \frac{X_2}{K_2} \right].$$

(14) By changing the bath temperature, T_B , different times, t , are determined. For two different bath temperatures, T_{B1} and T_{B2} , two times are determined, t_1 and t_2 , respectively.

(15) Since the system constant, B , is the same in either case, it is seen that, from Equation (24), a means of determining the ignition temperature is available, as shown by Equations (25) and (26).

$$t_1^2 (T_{B1} - T_s) = t_2^2 (T_{B2} - T_s) \quad \text{EQ.(25)}$$

Solving for T_s yields

$$T_s = \frac{t_1^2 T_{B1} - t_2^2 T_{B2}}{(t_1^2 - t_2^2)} \quad \text{EQ.(26)}$$

(16) From the data determined on a typical lot of 90% barium chromate - 10% boron ignition composition, as shown previously, letting $T_{B1} = 702^\circ\text{C}$, $T_{B2} = 682^\circ\text{C}$, $T_{B3} = 673^\circ\text{C}$, and $T_{B4} = 659^\circ\text{C}$, $t_1 = 25.6$ seconds, $t_2 = 35.6$ seconds, $t_3 = 39.4$ seconds and $t_4 = 73.5$ seconds, the following equation was used to determine ignition temperatures,

$$T_{s_i} = \frac{t_i^2 T_{B_1} - t_i^1 T_{B_2}}{t_i^2 - t_i^1} \quad \text{EQ(27)}$$

where $i = 2, 3, \text{ and } 4$.

(17) The ignition temperatures determined by this technique were

$$\begin{aligned} T_{s2} &= 660.5^\circ\text{C} \\ T_{s3} &= 651.8^\circ\text{C} \\ T_{s4} &= 653.0^\circ\text{C} \end{aligned}$$

which yields an average of $655.1^\circ\text{C} \pm 4.7^\circ$ as the ignition temperature of this sample.

7. Summary and Conclusions.

a. Summary.

(1) A theory is presented on the ignition of solid compositions. The effect of certain physical, chemical and thermal properties of a solid composition on the ignition time and ignition energy is explained and supported by experimental evidence.

(2) Different types of ignition systems are described. Problem areas of the normal ignition systems are discussed and a technique to overcome these problem areas is offered.

(3) By use of the developed ignition theory and a hot-bath immersion test apparatus, a technique of determining the true ignition temperature of a composition is described.

b. Conclusions.

The developed theory of ignition of solid compositions appears to offer the information required to understand the basic problem areas of ignition of solid compositions. The

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magnitude of the importance of the effects of ambient temperature, the thermal conductivity, density and specific heat of the solid composition, the rate of heat flow and the ignition temperature is clearly recognized from the developed equations.

Having this basic information available, new designs for ignition systems should no longer be hindered by the lack of knowledge of the important parameters involved in the ignition of pyrotechnic solid compositions.