

"INTRODUCTION TO PROGRAM SUBJECT - FIREPROOFING"

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Dr. Melvin Gerstein has conducted active research in the field of combustion related to fire hazards and propulsion systems for the past 20 years. This work has included research pertinent to aircraft and spacecraft fire hazards, safety in test and launch vehicles and combustion research in reciprocating, turbojet, ramjet and rocket engines.

Dr. Gerstein is currently involved in studies of aircraft fire hazards. He has been retained as a consultant on fire hazards in the Apollo and Manned Orbiting Lab spacecraft.

Prior to joining the University of Southern California, Dr. Gerstein was associated with NASA at the Lewis Research Laboratories in charge of advanced programs in propellant chemistry. His work as Assistant Propulsion Division Chief at NASA has resulted in major contributions to the basic understanding of jet propulsion design. Dr. Gerstein was also Division Chief in charge of physical science research at the California Institute of Technology, Jet Propulsion Laboratory.

Dr. Gerstein received both his Bachelor's and Doctorate at the University of Chicago in chemistry.

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It is a very real personal pleasure for me to introduce the technical portion of this symposium on fireproofing. It would seem logical to start by defining the term "fireproofing." Webster defines "fireproof" as "relatively incombustible," which doesn't really help us very much. Presumably we mean the development or treatment of materials to prevent or inhibit ignition, or to prevent or inhibit flame propagation. In a general treatment of fire safety, one would devote a great deal of effort in removing or isolating ignition sources. When dealing with the subject of fireproofing, however, we must assume that ignition sources exist. These may range from sparks to arcs, over-heated wires to large flames. In discussing fireproofing, it is necessary that we consider the nature of the ignition source - in fact, the nature of the total environment. A fireproof material under one set of circumstances may be readily combustible under another. Those who have been concerned with the hazards associated with high oxygen concentrations have certainly encountered materials which were fireproof in air, but burned readily in pure oxygen.

Fireproofing treatment initially, and widely used at the present time, consisted of treating materials with inorganic salts. Borates and phosphates are, and have been, widely used for this purpose. A simple test involving the application of a standard flame directly to the material can be used as illustrated in Figure 1. If the treatment has been successful, flame will not propagate away from the region of the torch and, when the torch is removed, flaming or glowing of the material will stop very quickly. The fireproofing additive, if a borate or phosphate or similar inorganic material, may interfere chemically with the free radical chemistry necessary for flame propagation. In addition, the low melting oxides of boron and phosphorus provide a barrier between the organic material and the ambient air. While the flame is being applied, it is possible that flammable vapors are released and consumed by the flame. If large amounts of flammable material were released, the flame would flare up, which is not desirable. If small amounts were released, the vapors would be consumed, and no additional hazard would be created.

Tests of this type have been used to rate materials. Let us consider, however, a different condition. In Figure 2, we assume that a source of heat

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is applied to the material indirectly, either by means of a flame, as shown, or some other heat source. The flammable vapors produced are not consumed by the flame and diffuse away from the surface creating a concentration gradient. Typical gradients for slow, intermediate and rapid gas evolution are illustrated in Figure III. In Figure IIIa, the rate of gas evolution is too lean to burn except very near the surface where surface quenching might inhibit ignition and flame propagation. An ignition source near the surface would not be a hazard. There may well be, as illustrated in Figure IIIb, an intermediate gas evolution rate which would produce a flammable mixture. Ignition could occur and a fire might continue to burn as long as the heat source was present to produce flammable vapor in spite of the fireproofing material which may be present. The fire occurs above the surface and the fireproofing material might not be effective if it is not vaporized. Although such a material might pass a flame test it would still represent a fire hazard in the presence of a less active heat source.

Finally, in Figure IIIc a very rapid gas evolution is illustrated. Such a situation may not present an ignition hazard near the surface but the large amounts of vapor produced could form flammable mixtures and ignite far from the surface. Flash fires resulting from smoldering fabrics are often the result of this type of behavior. A relatively fireproof material which does not itself ignite can release enough flammable vapor to create a hazard in the vapor space. The problem is compounded if the vapors released are also toxic or debilitating.

These experiments have considered an external ignition source. The heat source itself may also be the source of ignition. Figure II could easily have represented a thermal ignition experiment. Here, too, the problem is quite complex since two gradients are involved, a concentration gradient and a temperature gradient. Some of the important factors are illustrated in Figure IV. The upper curve is a plot of the ignition temperature of the vapor (T_{ig}) versus fuel concentration (F). It is assumed that some minimum temperature exists and that ignition becomes more difficult at higher and lower fuel concentrations. The solid line in the lower curve represents a fuel concentration (F) curve versus height above the surface. On the basis of the T_{ig} vs F and h vs F curves it is possible to generate a curve shown as a dotted line

which represents the required ignition temperature at any point above the surface. The ordinate remains height above the surface, h , and the abscissa becomes T_{ig} . If the actual temperature due to the heat source exceeds T_{ig} at any point, ignition will occur. In Figure IV, if the fuel gradient curve had been a temperature gradient curve, ignition would have occurred. Once ignited, of course, the flame might propagate over the entire sample. Since both fuel and temperature gradients are important it is easy to see that such an experiment would be quite sensitive to rate of heating, heat transfer rates, diffusion rates and other experimental variables.

The problem becomes even more complicated if there is a flow across the surface. One example from the work of Gerstein and Hyde (Ref 1) is illustrated in Figure V. The configuration is illustrated schematically. It consists of an air flow of velocity V_{∞} parallel to the surface. The flammable vapor leaves the surface at right angles to the flow and to the surface at a velocity V_0 as a mass flow, $\rho_0 V_0$. The value of V_0 would depend on heating rate, for example and represents a quantitative measure of the rate of flammable vapor evolution. The lines indicate the existence of a flammable mixture at two different stations along the surface, 0.4 ft from the start and 1 ft from the start. For a given air velocity, 10 ft/sec, a higher gas evolution rate is required at 0.4 ft than at 1 ft. The boundary layer is thin at 0.4 ft and the air dilutes the mixture which is flammable further away. At any specific location, more heat or a greater gas evolution rate is required as the air flow velocity increases. Between the two curves there is a region where ignition could not take place if the material was small (0.4 ft) but could take place if the material were large. These calculations can easily be related to shorter materials and lower velocities so that the conclusions are general. It is evident that the occurrence of ignition is strongly dependent on the complete environment and not on any single factor. The fireproofing expert must take this into account and define the conditions under which his material or his treatment is applicable.

More recently, fireproofing techniques have involved the use of specially formulated polymers or additives of an organic nature combined with the plastic or fabric. The freon type halocarbons containing bromine, chlorine and fluorine have been used for this purpose and various halogenated monomers have been polymerized to form fireproof plastics. Depending upon the decomposition characteristics of the polymer and the relative release of fuel components and

inhibitor components, the preceding discussions may still be applicable. Other factors must also be considered. Some work of Gerstein and Stine (Ref 2) with mixtures of fuels and carbon tetrachloride is relevant. Consider the case of Figure 2 but assume that the vapors released consist of a mixture of fuel and inhibitor. Flammability limit curves such as illustrated in Figure VI result. We have plotted the partial pressure of inert or inhibiting material versus the partial pressure of fuel. At $P_{\text{inert}} = 0$ we would have the normal lean and rich flammability limits in the absence of inhibitor. At some value of P_{inert} and above all mixtures would be non-flammable. Figure VII shows how such a curve can be generated. If the initial material had a composition N_1 , heating of the vapor could generate the curve shown. At some stage, since the inhibitor comes off less rapidly than the fuel a flammable mixture results indicated by X. As the initial composition is changed, the behavior changes until finally a composition is reached at which ignition does not occur during the entire heating period. The sample of initial composition N_4 would be judged as non-flammable or fireproof. Examine Figure VIII to see what happens as this "non-flammable" mixture is diluted by air. Dilution reduces both P_{inert} and P_{fuel} but the ratio $P_{\text{inert}}/P_{\text{fuel}}$ remains constant. Dilution is represented by a straight line through the origin from the location of the final mixture. It is shown in Figure VIII by a series of arrows. The non-flammable mixture crosses into the flammable range and ignition is possible. Again, the purpose of this example has been to emphasize the importance of defining the exact conditions of the test and environment before the labels of fireproof or non-flammable are applied.

I have not tried to summarize the large body of literature on fireproofing. Rather I have taken advantage of the prerogative of an introductory speaker to raise questions rather than answer them. Specifically I have tried to emphasize the great importance of defining the exact conditions under which a material is fireproof and the awareness that "fireproof" materials can burn or lead to fires under conditions different from those evaluated by a single test. I have not touched on the many other problems faced by the

fireproofing experts including the physical and structural properties of the materials, possible toxic gases released by thermal decomposition, cost and fabrication difficulties. The papers which follow illustrate that major progress has been made in the field of fireproofing. Much more still needs to be done.

REFERENCES

1. Gerstein and Hyde, "A Boundary Layer Model For Pilot Ignition of Cellulosic Solids in a Wind (to be published). Based on Engineers Degree Thesis, August 1970, University of Southern California.
2. Gerstein and Stine, "Anomalies in Flash Points of Mixtures of Halogenated Hydrocarbons and Flammable Liquids (to be published).

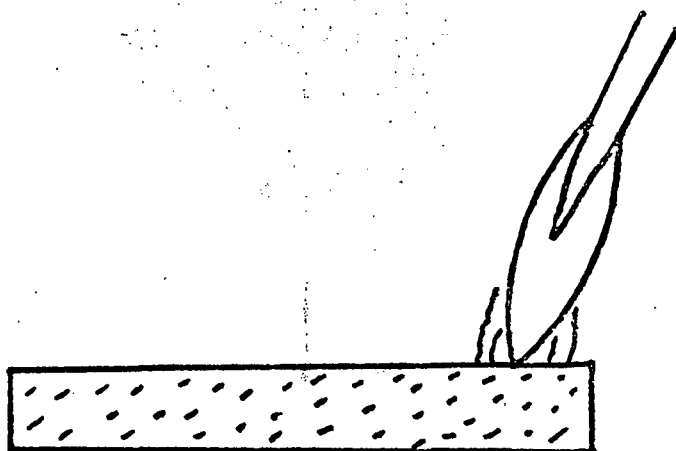


Figure I. Simple Flame Test

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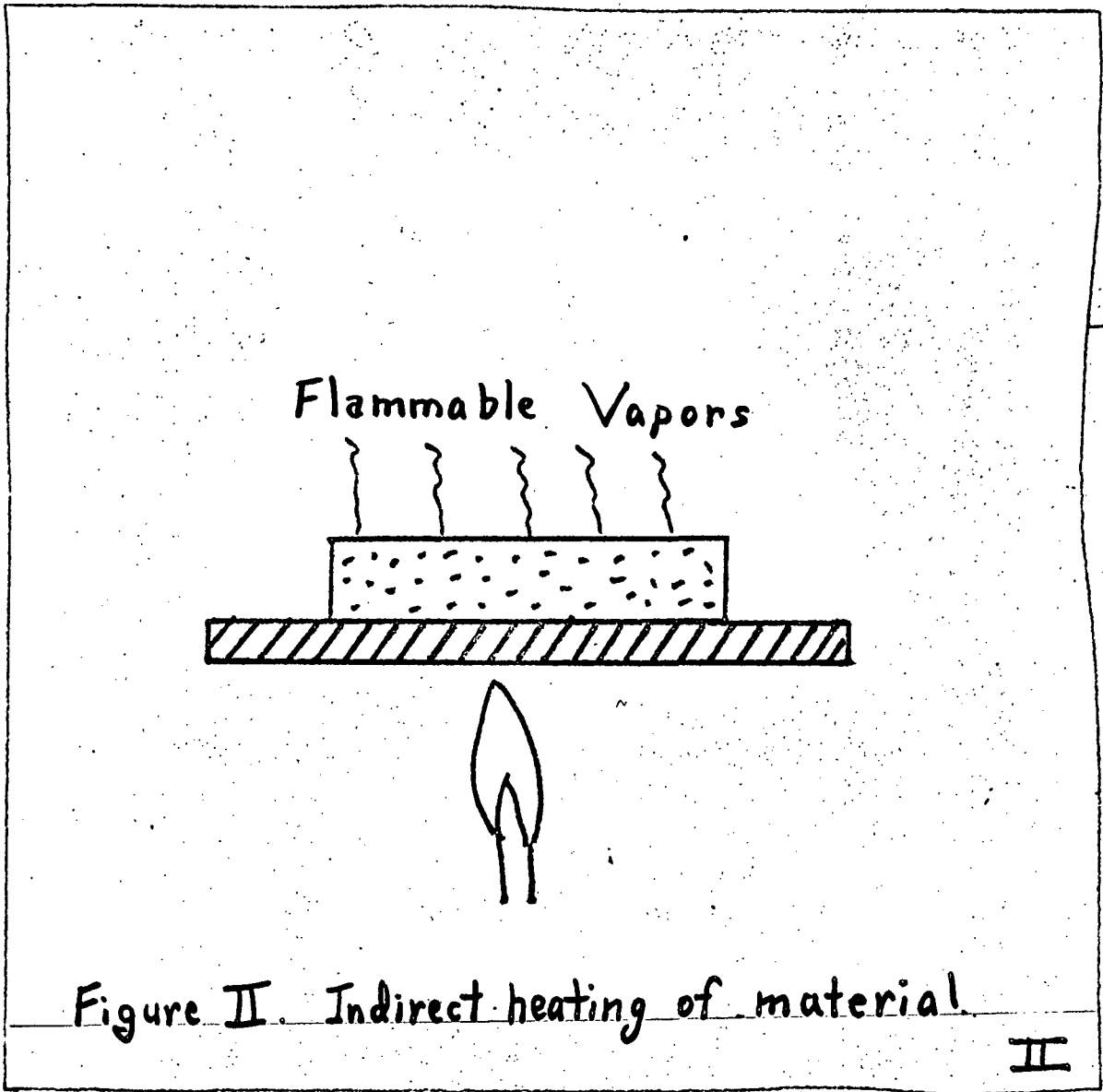


Figure II. Indirect heating of material.

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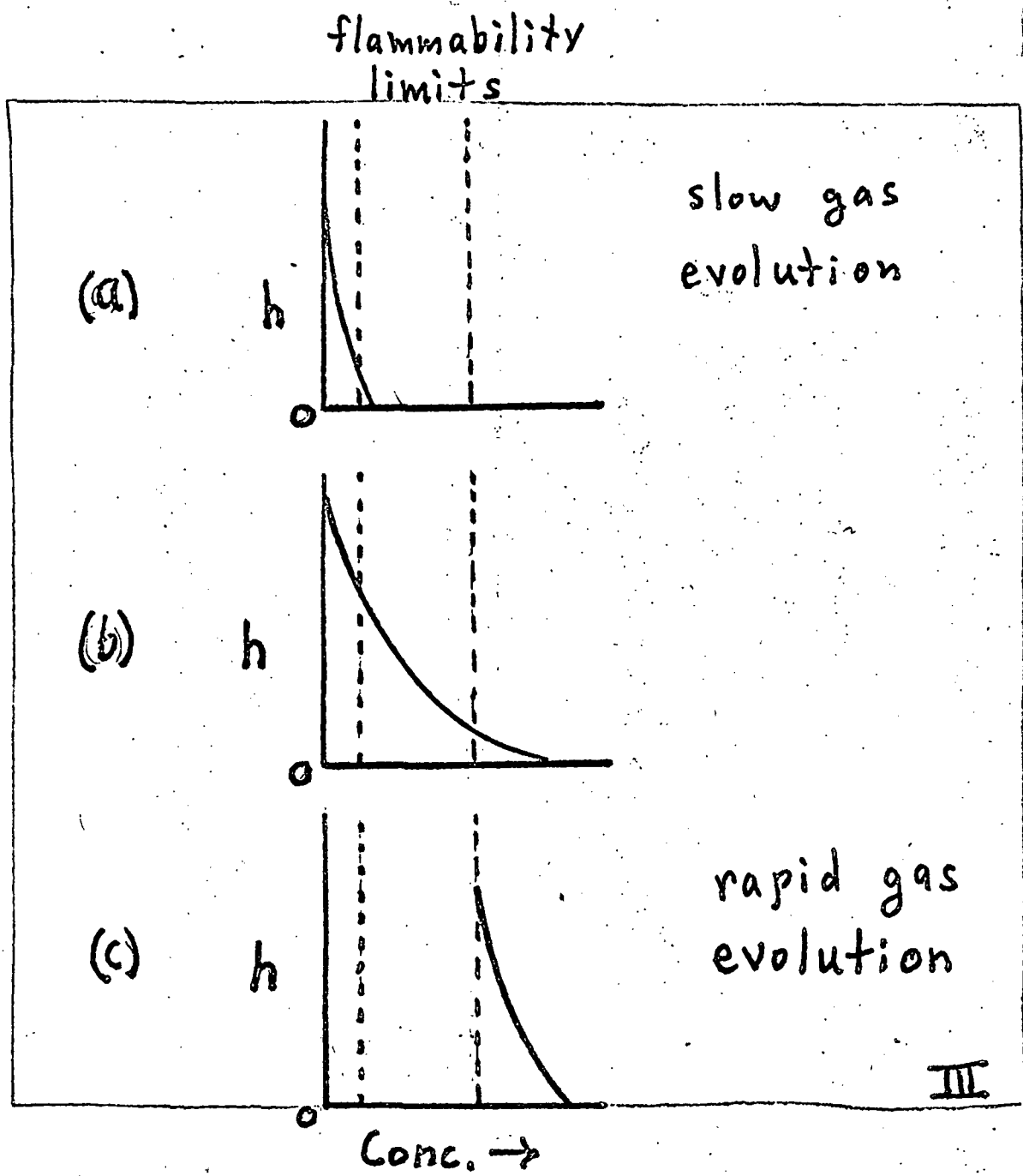


Figure III. Concentration Gradients near a Heated Surface

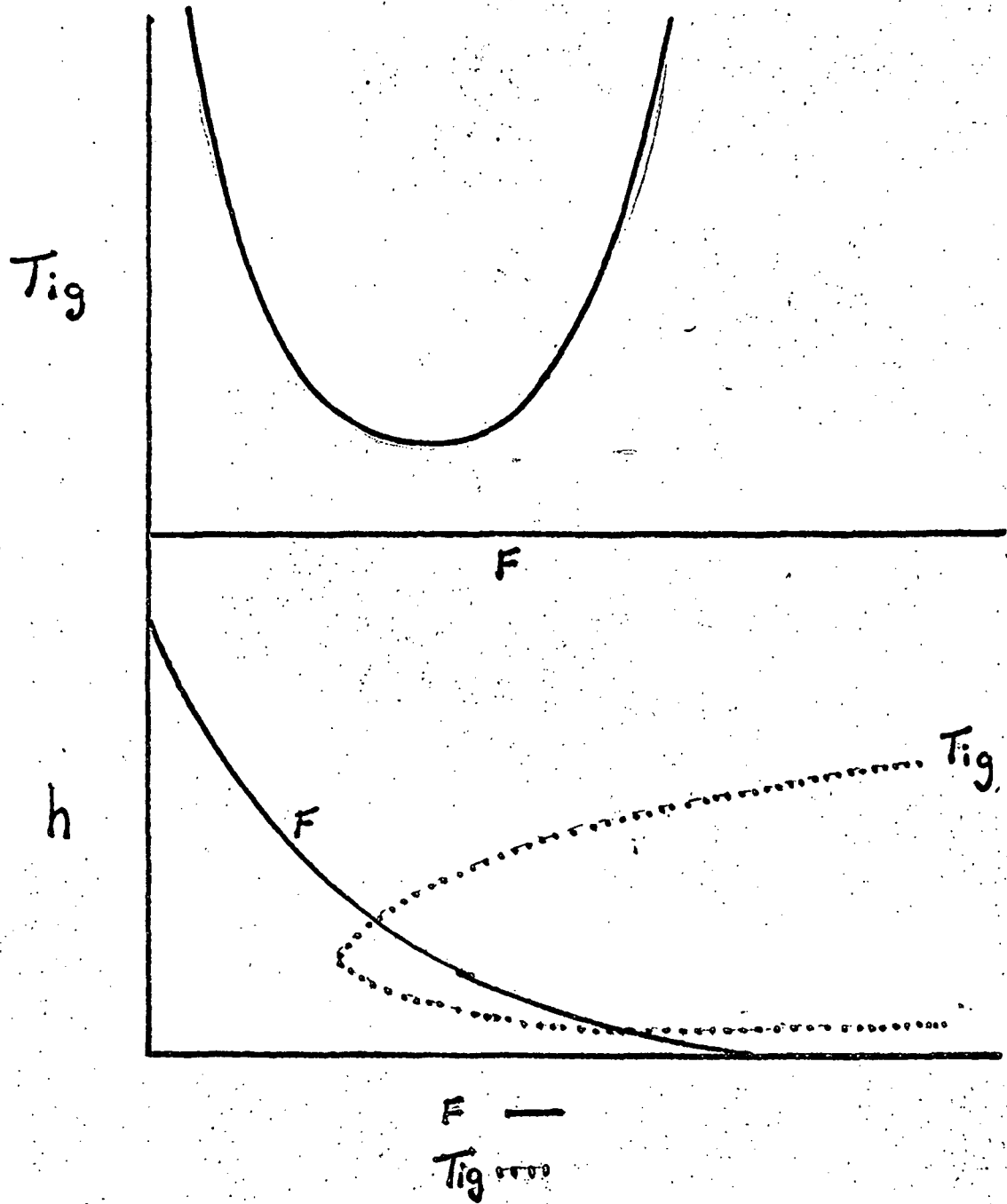
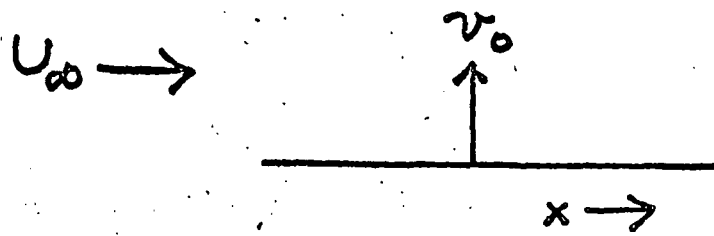


Figure IV. Thermal Ignition Conditions



v_0
Fuel Velocity
ft/sec

critical mixture
curves

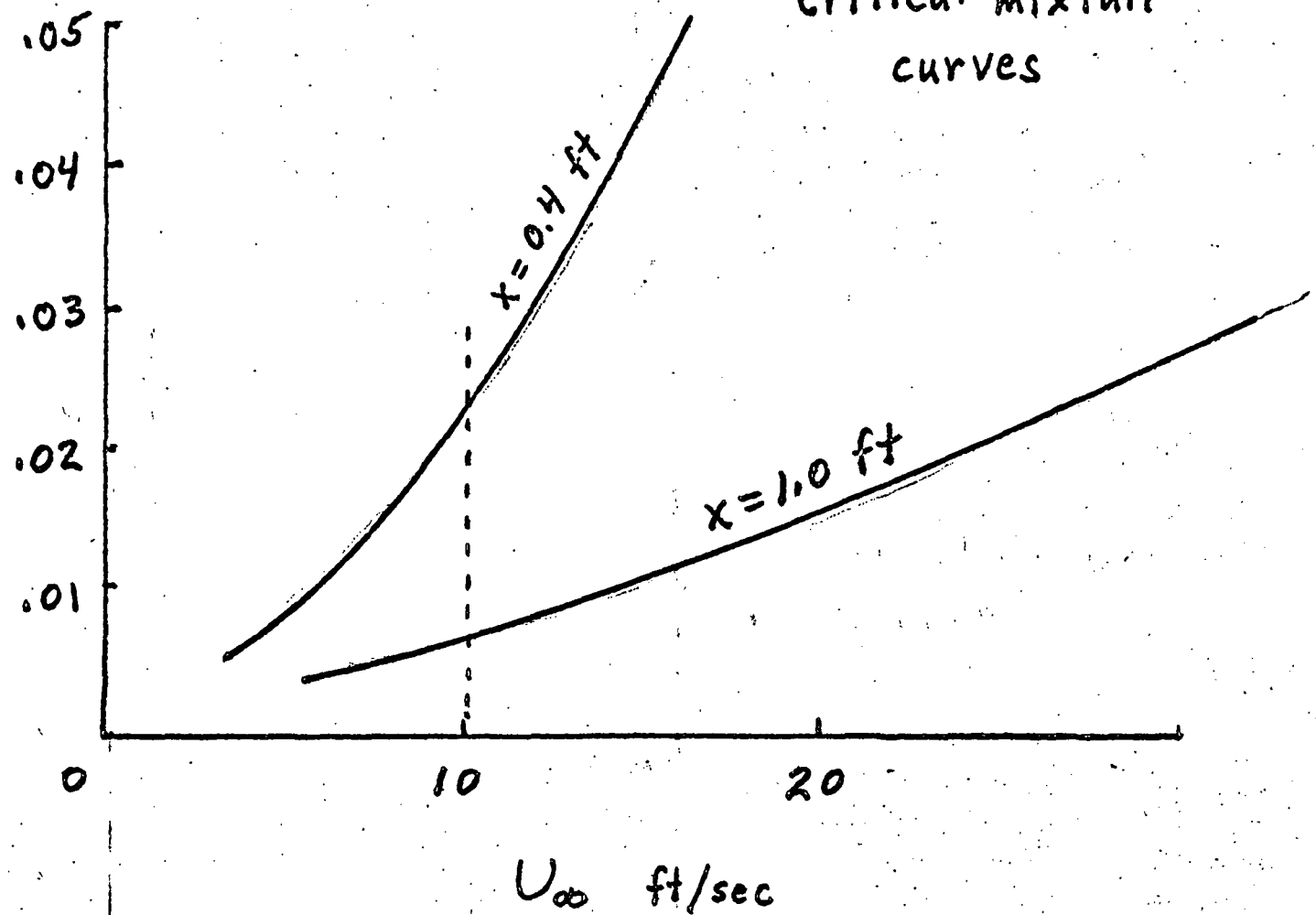
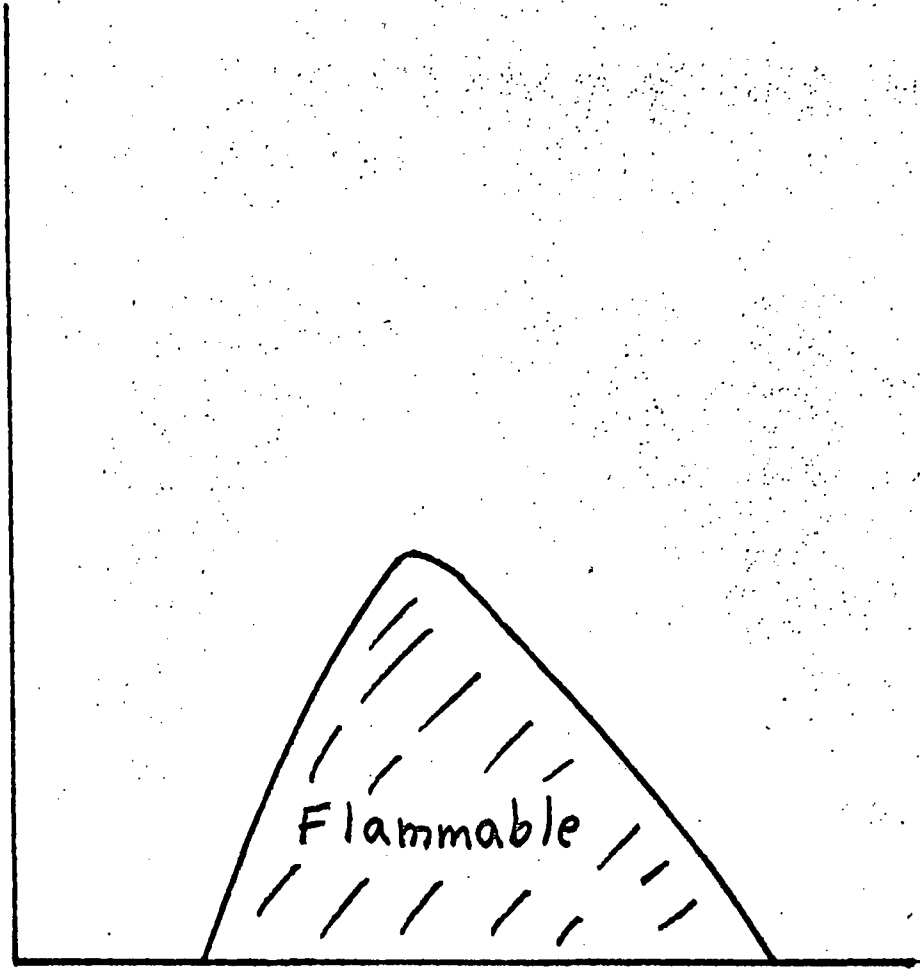


Figure V. Effect of flow on formation of Critical (flammable) Mixtures.

P_{INERT}



P_{FUEL}

Figure III. Flammability Limit Curve

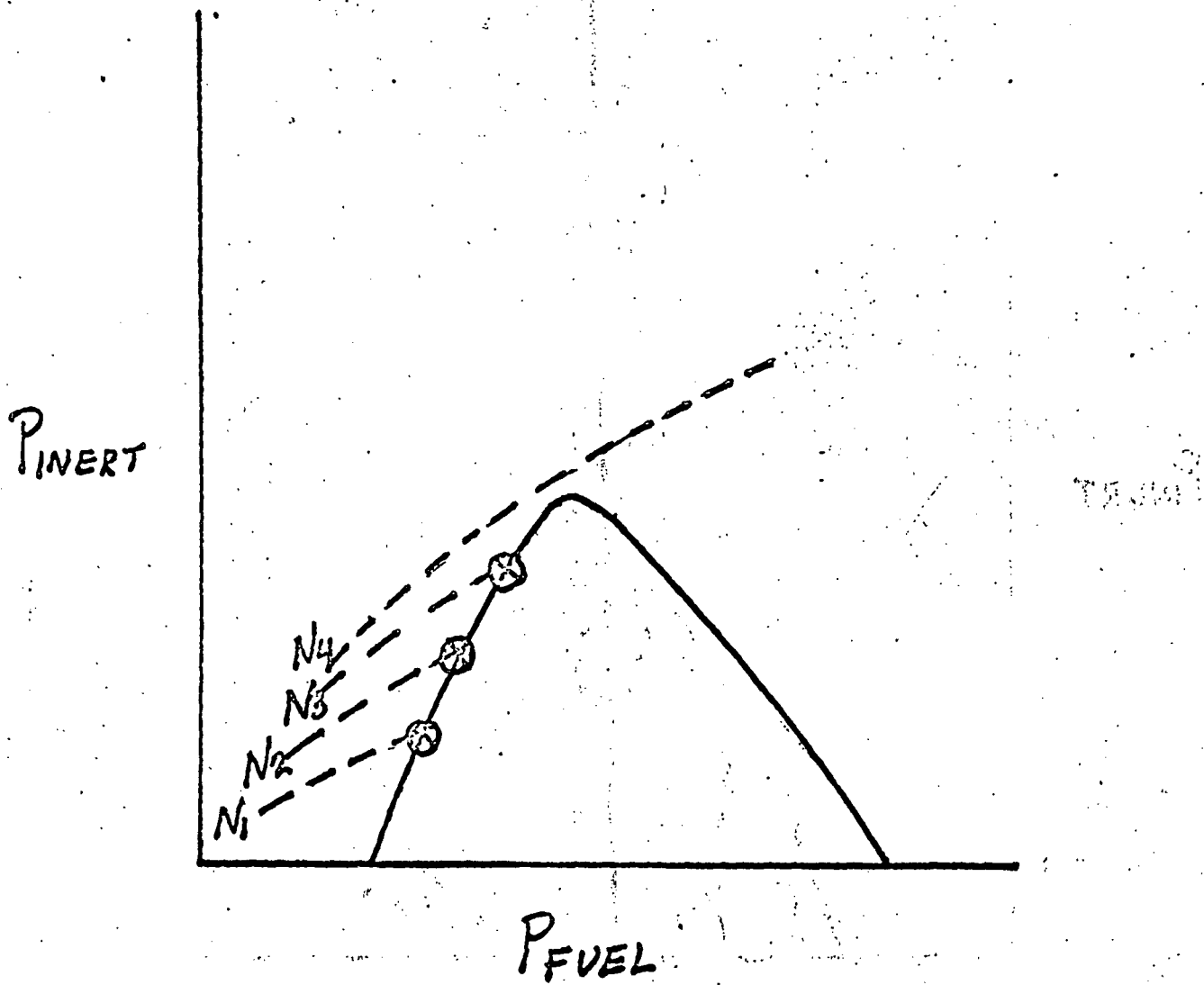


Figure VII Generation of Flammability Curve

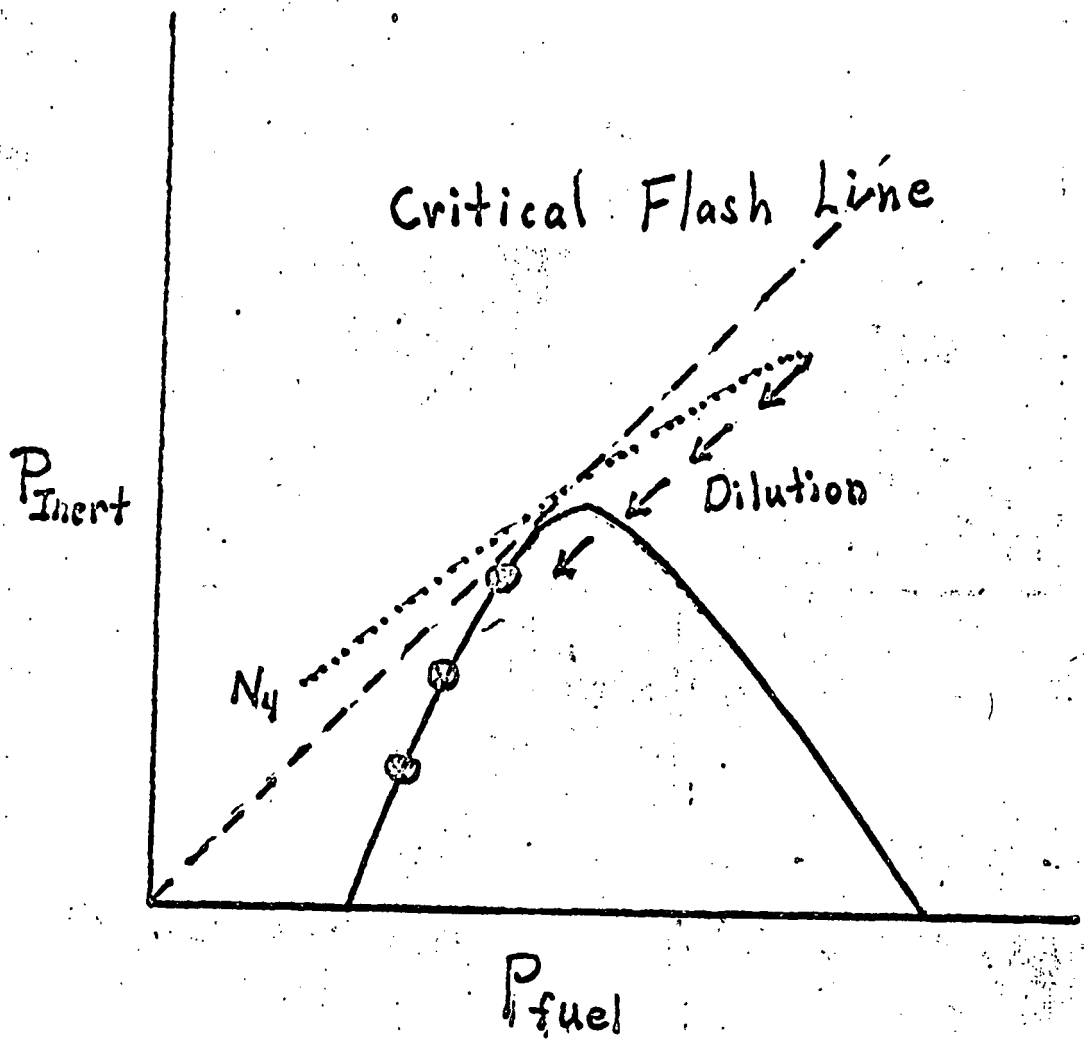


Figure VIII. Dilution Effects which make a non-flammable mixture - flammable