# Correlation of Liquid Propellant Impact Sensitivity with Entrapped Gas Thermal Diffusivity

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**Experimental impact sensitivity data have been obtained for normal propyl nitrate as the condensed phase with gas bodies consisting of single component systems, binary systems, and a ternary system. The experimental program has separated (for the first time) the effects of heat capacity ratio, thermal conductivity, and chemical reactivity of the gas body on the impact sensitivity. Based upon a theoretical model of initiation proposed, the impact sensitivity of *n*-propyl nitrate has been correlated with the thermal diffusivity of the entrapped gas body. The effect of chemical reactivity of the gas body has been demonstrated.**

IMPACT testing is a simple and rapid means for determining the explosion hazard of propellant materials. In the standard test, a sample of the liquid propellant is placed in a cup which is fitted with an O-ring. A 0.016-inch thick stainless steel diaphragm is placed on the O-ring, and a vented piston supports a steel striker ball. Impact is delivered to the ball by a freely falling weight. The impact energy is increased until an explosion occurs and the diaphragm ruptures.

Investigations of the mechanism of the impact initiation process have been carried out since World War II by a large number of investigators (*1–3, 5, 7–12*). The initiation process occurs within an interval of the order of $10^{-4}$ seconds (*2*). The time to initiation represents an initial delay (before any visible reaction), the propagation of a slow flame at velocities of 10 to 50 meters per second, and the explosion. The explosion may propagate at velocities of several meters per second or may develop into low order detonation and propagate up to 2 kilometers per second.

The basic premise upon which initiation theory is developed is that the propellant is raised rapidly to some high temperature; Bowden (*2*) has proposed various processes by which this may be accomplished.

Bowden and Yoffe (*1*) have further proposed that the mechanism of initiation in liquid explosives by impact is due to the formation of local hot spots of the order of 500° C. rather than homogeneously throughout the body of the sample. The hot spots are raised to a high temperature by the unequal distribution of the energy of impact.

The exact mechanism of formation of the hot spots may not always be the same since several processes are possible and one or more might operate simultaneously. Probably the most likely mechanism for hot spot production in liquids is the rapid compression of entrapped gas bodies. Transferring the liquid propellant from one container to another will entrap some air; and there exists the possibility of absorption of minute quantities of air, $CO_2$, etc. upon standing and subsequent release of microscopic bubbles upon heating slightly. Also, with some types of testing equipment, bubbles may be entrapped by microscopic cavities in the striker at the instant of impact.

Whether the hot spot grows into a large scale explosion or dies out is determined by the strength of the impact, physical state of the system, thermodynamic properties of the materials, and kinetics of the decomposition reaction. Johansson and Selberg indicate that the increase in temperature around a gas body owing to heating from the compressed gas is only a fraction of that owing to the gas temperature rise, and for ignition to occur droplets must be dispersed into the gas phase (*5*).

The classical theory of initiation by adiabatic compression as proposed by Bowden and Yoffe (*1*) provides a mechanism whereby a hot spot may develop in the liquid phase. An examination of the impact data for various gas bodies reported in the literature shows that the classical theory fails to provide information as to whether a given material under a given impact condition will be more or less sensitive than another material subjected to the same conditions.

## EXPERIMENTAL

**Equipment.** DROP-WEIGHT TESTER. An Olin-Mathieson Drop-Weight Tester, Model 830–700 was supplied by the Air Force. Figure 1 shows details of the sample cup assembly. The liquid sample is confined in the cavity formed by the steel cup, the rubber O-ring, and a stainless steel diaphragm placed over the O-ring. Since the volume of the cavity is fixed, variations in the sample volume must result in variations in the gas body size. The total heat released in the bubble during compression is a function of the initial volume since the energy absorbed by the bubble equals the work done on the system—i.e., $P\Delta V$. Therefore a standard

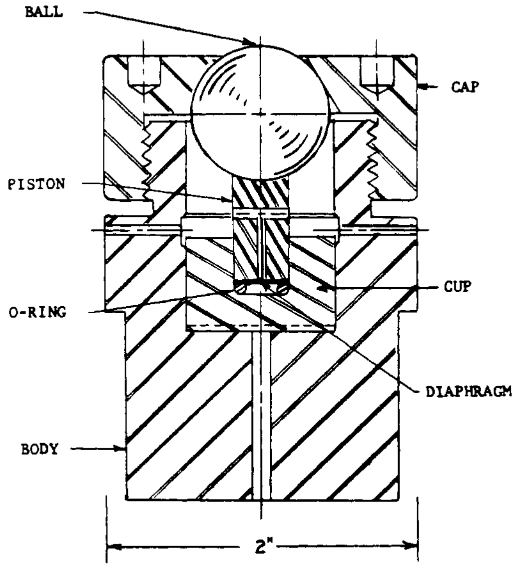

Figure 1. Sample cup assembly

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quantity of sample was used throughout all tests; a fixed stroke Hamilton Microliter syringe with a Chaney adaptor was used to deliver the sample. An accuracy of 0.01% liquid discharge was possible.

Atmosphere Box. A controlled atmosphere box was used for filling the sample cup assemblies under the various gaseous atmospheres. Weather ballons, used as positive displacement devices, were filled with compressed air until the box was essentially filled. Then fresh gas of the atmosphere being used was admitted to the box directly from a premixed tank as the ballons were allowed to collapse. The box was maintained under a positive pressure of 1 to 2 inches of water to ensure that no air entered the system.

Temperature Control Circuit. The standard test procedure (*6*) calls for testing to be performed at 68 ± 2° F. The temperature control circuit consisted of a low vapor pressure oil bath which was placed inside the atmosphere box. Oil circulated from the internal bath through a coil which was immersed in an external ice bath and then back to the internal bath. A copper tray immersed in the internal oil bath received the sample cup assembly.

The standard loading and handling procedure adopted was to cool the sample cup assembly to 69° F. and then to load it with pre-cooled sample. The loaded cup assembly was transferred to the tester and impacted immediately.

**Materials.** Properties of Materials. *N*-propyl nitrate, obtained from Eastman Organic Chemicals, was purged with nitrogen gas (99.996% purity) for 10 hours to remove traces of oxygen and then stored under a blanket of nitrogen. Gases were purchased from the Mathieson Co. with a minimum purity as shown: argon, 99.998%; helium, 99.99%; nitrogen extra dry grade, 99.7%; oxygen extra dry grade, 99.6%; and Freon-12, 99.0%. No further purification was attempted.

**Procedure.** Calibration of the Apparatus. The standard procedure for calibration of the instrument was to determine the impact energy required to produce the 50% probability point for hydraulic rupture of the stainless steel diaphragm under the same conditions used in propellant testing. The value obtained established the upper working limit for the particular diaphragm since rupture occurs at this point irrespective of the explosive ability of the material being tested.

Table I. Impact Sensitivity Data for Normal Propyl-Nitrate under a Helium Atmosphere

Sample volume, 0.03 cc.; sample temperature, 69° F.; ambient temperature, 73° F.; height, 20 cm.

| Test No. | Weight, Kg. | Energy, Kg.-Cm. | Result |
|---|---|---|---|
| 1 | 2.90 | 58 | – |
| 2 | 2.95 | 59 | +[a] |
| 3 | 2.90 | 58 | – |
| 4 | 2.95 | 59 | – |
| 5 | 3.00 | 60 | – |
| 6 | 3.05 | 61 | + |
| 7 | 3.00 | 60 | – |
| 8 | 3.05 | 61 | + |
| 9 | 3.00 | 60 | – |
| 10 | 3.05 | 61 | + |
| 11 | 3.00 | 60 | – |
| 12 | 3.05 | 61 | – |
| 13 | 3.10 | 62 | – |
| 14 | 3.15 | 63 | + |
| 15 | 3.10 | 62 | – |
| 16 | 3.15 | 63 | + |
| 17 | 3.10 | 62 | – |
| 18 | 3.15 | 63 | + |
| 19 | 3.10 | 62 | + |
| 20 | 3.05 | 61 | – |

[a] Burned—smoke but no rupture. Arithmetic mean = 1216/20 = 60.80. $E_{50}$ = 60.80 kg.-cm.

Values obtained ranged from 108.1 to 108.5 kg.-cm.; these are lower than those shown in JANAF Test Methods No. 4 (*6*) but are more nearly constant values (129 to 148 for JANAF data). The upper limit for testing was then established at 92 kg.-cm. (85% of rupture value) in accordance with established procedures.

Test Procedure. All tests were run in accordance with the procedure recommended by the JANAF Test Methods No. 4 (*6*, p. 4).

The energy required for initiation of explosion is not a sharply defined point by the impact test; however, the occurrence of explosion follows a normal distribution over the range of energy levels. The sensitivity value reported is the mean value or the point of 50% probability of an explosion occurring. The 50% point ($E_{50}$) was readily established by making a number of determinations bracketing the 50% point by changing the energy level after each test. When the test was positive, the weight was decreased and vice versa.

Drop heights of 10 and 20 cm. were used in these experiments. When 20 tests had been performed, the 50% point was computed by a simple statistical analysis of the distribution of test results. A typical set of the raw experimental data is shown in Table I; all data taken have been recorded (*7*) and are summarized in Table II.

## ANALYTICAL MODEL

The ideal analytical model is that of a single spherical gas bubble immersed in an infinite reservoir of the liquid propellant. A series of events is postulated to take place when the system is subjected to impact: the gas-liquid interface moves in as the bubble is compressed, the gas temperature rises owing to compression, reaction occurs at an increasing rate, and vaporization occurs at the gas-liquid interface and the interface recedes as the explosion occurs. For simplicity, it is assumed that impact occurs instantaneously; this is equivalent to stating that the gas body is suddenly subjected to a step in temperature. Let $\rho_g$, $C_{pg}$, $k_g$, and $\alpha_g$ be the thermal constants and $T_g$ be the temperature of the gas phase; also let $\rho_l$, $C_{pl}$, $k_l$, and $\alpha_l$, be the thermal constants and $T_l$ be the temperature of the liquid phase.

Table II. Impact Sensitivity Data for Normal Propyl-Nitrate

| Gas Body | | Sample | Mean $E_{50}$, |
|---|---|---|---|
| Inert | Oxygen, % | Temp., ° F. | Kg.-Cm. |
| Argon | None | 71 | Above 92 |
| Helium | None | 69 | 60.80 |
| | 4 | 69 | 59.35 |
| | 13 | 69 | 50.13 |
| | 17 | 69 | 30.15 |
| | 21 | 69 | 15.02 |
| | 50 | 69 | 13.10 |
| Nitrogen | None | 69 | Above 92 |
| | 4 | 69 | Above 92 |
| | 13 | 69 | 83.80 |
| | 17 | 69 | 59.70 |
| | 21 | 69 | 16.95 |
| | 50 | 69 | 16.53 |
| Freon | None | 69 | Above 92 |
| | 18 | 69 | Above 92 |
| | 21 | 69 | Above 92 |
| | 50 | 69 | Above 92 |
| Freon/He (10/73) | None | 69 | 72.85 |
| | 13 | 69 | 62.65 |
| | 17 | 69 | 39.00 |
| | 21 | 69 | 29.43 |
| | 50 | 77 | 9.45 |
| A59.6%/He40.4% | None | 69 | 78.30 |
| None | Air | 70.5 | 16.95 |
| | Air | 77.0 | 15.13 |
| | Air | 99.0 | 11.75 |

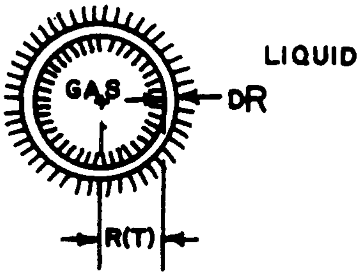

Figure 2. Moving interface

Suppose λ is the latent heat of vaporization and $T_v$ the temperature of vaporization on the liquid propellant; if the surface of separation between the gas and liquid phases is at $R(t)$, one boundary condition to be satisfied at this surface is $T_g = T_l = T_v$ when $r = R(t)$.

The second boundary condition concerns the adsorption of latent heat at this surface. The region $r < R(t)$ contains gas at temperature $T_g(r, t)$. When the surface moves a distance d$r$, a quantity of heat $\lambda\rho$ d$R$ is adsorbed and must be supplied by conduction (*4*) (Figure 2).

This requires:

$$k_g \frac{\partial T_g}{\partial r} - k_l \frac{\partial T}{\partial r} = \lambda \rho_l \frac{\mathrm{d}R}{\mathrm{d}t} \qquad r = R \quad (1)$$

Division by $C_{pg}\rho_g$ yields:

$$\alpha_g \frac{\partial T_g}{\partial r} - \frac{k_l}{C_{pg}\rho_g} \frac{\partial T}{\partial r} = \frac{\lambda \rho_l}{C_{pg}\rho_g} \frac{\mathrm{d}R}{\mathrm{d}t} \qquad (2)$$

In the gas and liquid phases, the temperatures must satisfy:

$$\frac{\partial T_g}{\partial t} - \alpha_g \left( \frac{\partial^2 T_g}{\partial r^2} + \frac{2}{r} \frac{\partial T_g}{\partial r} \right) - qAe^{-E/\mathrm{R}(T_g - T_o)} = 0 \quad r < R \quad (3)$$

$$\frac{\partial T_l}{\partial t} - \alpha_l \left( \frac{\partial^2 T_l}{\partial r^2} + \frac{2}{r} \frac{\partial T_l}{\partial r} \right) = 0 \qquad r > R \quad (4)$$

where $q$ is the heat of reaction per unit mass and $Ae^{-E/RT}$ is the Arrhenius expression for the reaction rate. A complete description of the system requires the simultaneous solution of Equations 1, 3, and 4; numerical methods are necessary because of the heat generation term. Examination of Equations 2 and 4 shows that, for a given liquid propellant, the gas properties control the rate of transfer of energy at the interface. Therefore, different entrapped gas bodies must require different impact energies for explosion initiation. A characteristic thermal property is the thermal diffusivity which appears in Equations 2, 3, and 4. The impact energy required for initiation of explosion should correlate with the thermal diffusivity of the entrapped gas body when a given liquid propellant is subjected to impact with different entrapped gas bodies. This has been done in Figure 3 where the mean impact energy ($E_{50}$) has been plotted *vs.* the thermal diffusivity of the entrapped gas body for the series of gases tested in the experimental program. Clearly a correlation exists.

## DISCUSSION

An analysis of the impact data reported in the literature shows that initial pressure of the gas body is universally important. This is in agreement with the classical theory which postulates that initiation is due to adiabatic compression of entrapped gas bodies:

$$\frac{T_2}{T_1} = \left( \frac{P_2}{P_1} \right)^{\frac{\gamma - 1}{\gamma}}$$

The equation states that an increase in the pressure ratio for a given initial temperature increases the final temperature; likewise an increase in the initial temperature for a given pressure ratio increases the final temperature and the higher the final temperature the more likely the explosion. This is about all that can be concluded from the classical theory. Clearly an additional mechanism is needed.

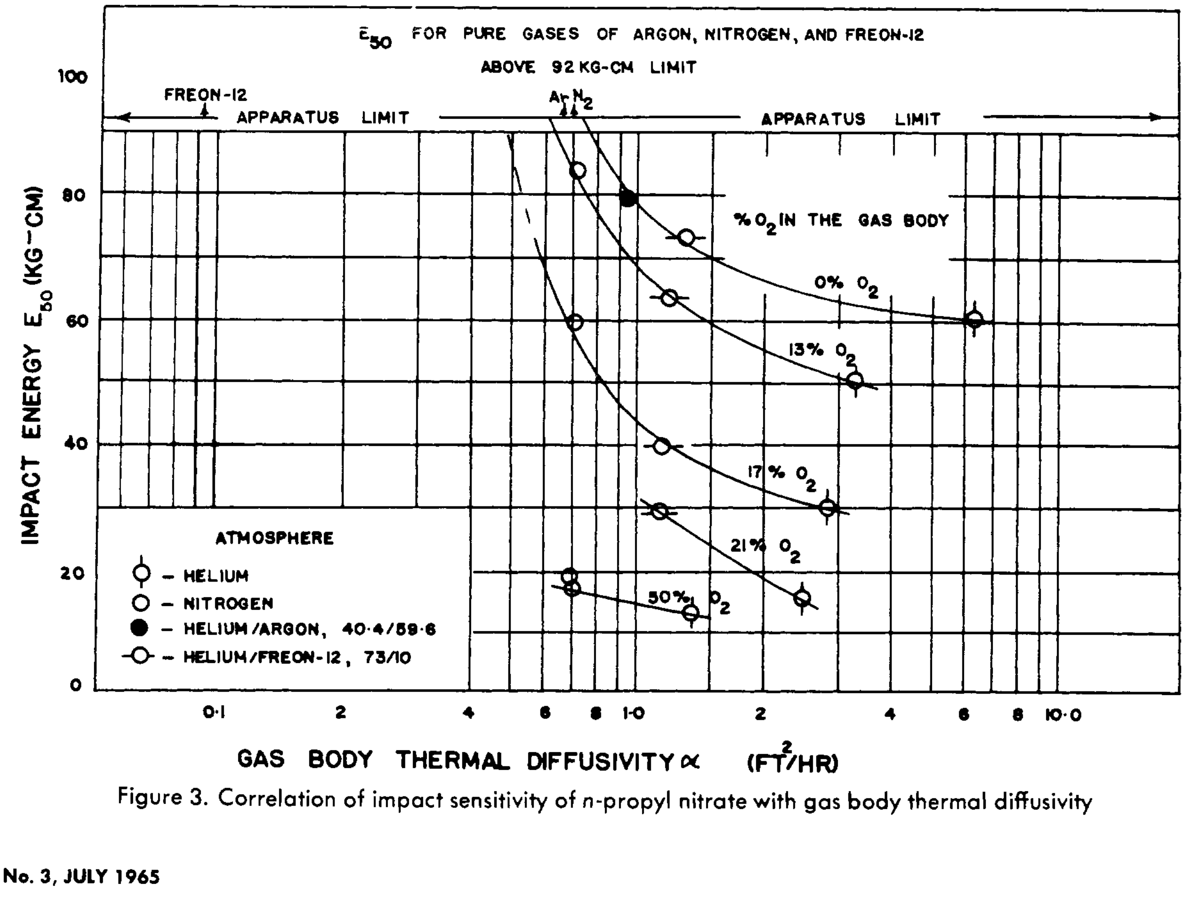

Figure 3. Correlation of impact sensitivity of *n*-propyl nitrate with gas body thermal diffusivity

The mechanism proposed retains the hot spot concept, but relaxes the adiabatic requirements and considers the thermal characteristics of the entrapped gas. Under conditions of impact, the temperature of the entrapped gas body rises rapidly and essentially adiabatically creating a hot spot or kernel. Classical theory further implies that it occurs isentropically, but this is not necessarily so since shock waves probably develop. Some chemical reaction also occurs during the compression step (some propellant is present in the gas phase owing to vapor pressure, and some droplets or ligaments are probably dispersed into the gas phase when impact occurs), and this increases the kernel temperature. The hot gas body vaporizes liquid propellant at the gas-liquid interface. For an explosion to progress throughout the system, sufficient heat must be supplied by the kernel to vaporize and heat to ignition temperature the differential shell of liquid surrounding it; this shell burns and liberates heat to continue the process in the next shell and so on. The vaporization process requires a large amount of energy; this energy must initially come from the hot spot. Therefore, the rate of heat transfer through the gas body must be sufficiently large to accomodate the initial vaporization process. If the heat is transferred by pure conduction, then the rate of transfer is determined by the thermal diffusivity of the gas body for a given liquid system. The thermal diffusivity of the gas body, then, may be used as a means for ranking the sensitivity of a given liquid propellant to various inert atmospheres. The higher the thermal diffusivity of the gas bubble, the greater the sensitivity of the liquid to impact. If a given liquid propellant is subjected to impact under two different atmospheres of the same thermal diffusivity, the more reactive one will initiate explosion at the lower impact energy level.

These conclusions are borne out in Figure 3. On the basis of the correlation, it is predicted that each of the pure gases argon, nitrogen, or Freon-12 would have $E_{50}$ values above the 92 kg.-cm. limit established for the drop-weight tester used. This was found to be the case experimentally. The data also illustrate again the inadequacy of the classical theory since helium and argon both have heat capacity ratios of 1.67 and are inert gases. Helium, however, initiates explosion readily whereas argon does not. The correlation correctly confirms this also.

The same reasoning applies in the liquid phases; here, however, the lower the thermal diffusivity the more sensitive the system should be—a high thermal diffusivity would dissipate the energy into the liquid without vaporization and ignition of the interface.

The effect of chemical reactivity is also shown in Figure 3. Curves of constant per cent oxygen show that increasing oxygen content—i.e., increasing chemical reactivity of the mixture—in the gas body increases the sensitivity to impact. This is readily explained by the fact that the hot spot temperature (as well as shells subsequently ignited) will be increased by increased oxygen concentration in the gas phase until a stoichiometric mixture results. Further increases in oxygen concentration would then have about the effect of additional nitrogen since the thermal diffusivities are so close.

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## NOMENCLATURE

$c_p$ = specific heat
$E$ = activation energy
$P$ = pressure
$q$ = heat of reaction
R = universal gas constant
$T$ = temperature
$t$ = time
$u$ = velocity
$R$ = distance
$\alpha$ = thermal diffusivity
$\gamma$ = specific heat ratio
$\lambda$ = latent heat of vaporization
$\rho$ = density

### Subscripts

$l$ = liquid
$g$ = gas
$v$ = vaporization

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