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NAVORD REPORT 6126

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A CORRELATION OF IMPACT SENSITIVITIES OF EXPLOSIVES WITH OXIDANT BALANCES

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U. S. NAVAL ORDNANCE LABORATORY
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This report describes a hitherto explicitly unnoticed relationship between impact sensitivities of explosives or explosive mixtures and their oxidant balances. The consequences of this relationship are explored. If the relationship noted herein is valid, as this limited study indicates, a new direction for improved performance explosive research is indicated which may result in greater safety. The work described in this report was performed under Task No. 800-667/76004/01.

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By direction

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A CORRELATION OF IMPACT SENSITIVITIES OF EXPLOSIVES WITH OXIDANT BALANCES

INTRODUCTION

The impact sensitivity of an explosive varies to an extent depending on the operator, the preparation and condition of the impact sample and multifold other, as yet undetermined, causes. Thus it is at present possible to distinguish only gross differences in sensitivity between structurally similar organic compounds. The present study was undertaken with the purpose of establishing a relationship whereby we might judge how the impact sensitivities of a recently prepared series of compounds containing the terminal fluorodinitromethyl group (1) compared with other polynitroaliphatic compounds at similar levels of "explosive power." In developing the relationship herein described it soon became apparent that there might be ramifications extending far beyond this original limited objective.

In view of the unreliability of any individual impact result it appeared that any correlation would necessarily be based on a large number of impact sensitivities determined for a wide variety of compounds. Our hope was that errors would average out and that a plot of these impact results as a function of whatever parameter were chosen for comparison would show distribution around a "true trend." The trend would then serve as a tool for predicting variation of impact behavior with the chosen parameter.

The parameters chosen for comparison were logarithm of 50% impact height as determined on the ERL machine and Oxidant Balance per 100 grams of explosive. Impact heights were determined for 30/50 sieve cuts using Type 12 tools on sandpaper. The other quantity, abbreviated as OB/100, is defined as the number of equivalents of oxidant per 100 g of compound above the amount necessary to burn all hydrogen to water and all carbon to carbon monoxide.*

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* The term "Oxidant Balance" rather than the more conventional "Oxygen Balance" is used to conform with the current trend in explosives technology toward incorporation of oxidants other than oxygen in explosive molecules.

In calculating OB/100 an atom of oxygen represents two equivalents of oxidant per mole, an atom of fluorine one equivalent. Hydrogen represents one equivalent of reductant, carbon two equivalents. Since carboxyl groups are considered as "dead-weight", two equivalents of oxidant per mole are subtracted for each such group in the molecule. For compounds containing only carbon, hydrogen, nitrogen and oxygen, the applicable equation is

$$OB/100 = \frac{100\ (2\ n_O - n_H - 2\ n_C - 2\ n_{(-COO-)})}{\text{Mol. Wt.}}$$

where n_O, n_H and n_C represent the number of atoms of oxygen, hydrogen and carbon in the molecule and $n_{(-COO-)}$ the number of carboxyl groups.

For compounds balanced to the carbon monoxide level, OB/100 = 0. Above the CO level, OB/100 has a positive sign, below the CO level a negative sign. For *bis*-trinitroethyl 4,4-dinitropimelate, a compound whose molecular formula is $C_{11}H_{12}N_8O_{20}$ and which contains two carboxyl groups, the calculation is as follows:

$$OB/100 = \frac{100\ (40 - 12 - 22 - 4)}{576} = + 0.35$$

An attempt was made to eliminate the possibility that preformed prejudices might unconsciously influence the choice of examples. The first one hundred compounds encountered in a random search of a comprehensive card file maintained by Dr. O. H. Johnson of the Chemical Engineering Division and the periodic NavOrd Reports listing sensitivities of explosive samples received by the Explosives Properties Division (2) during the period 1 January 1950 to 1 November 1956 were taken. The following criteria were then set for inclusion: The compound (a) was solid at room temperature, (b) contained no heteroaromatic ring such as triazole, tetrazole, etc., (c) contained no acetylenic or azido groups and (d) was not a salt. Of the original hundred, eighty-four met all criteria.

RESULTS

These eighty-four compounds are listed in Table I together with the seven fluorodinitromethyl compounds whose impact properties it was our initial aim to evaluate. Listed also for each is the molecular formula, molecular weight, oxidant balance per mole, OB/100 and impact sensitivity. For convenience, the compounds are divided into categories as follows:

1. Eight compounds with nitrogen exclusively in nitramine linkages. Tetryl is included to avoid setting up a separate category for this single example.

2. Seven compounds with nitrogen in both nitramine and *gem*-dinitro groups.

3. Seventeen examples containing both nitramine and trinitromethyl linkages. Some also contain *gem*-dinitro groups.

4. Three compounds having nitramine and nitrate ester functions. They may also contain trinitromethyl or *gem*-dinitro.

5. Ten nitramides, all having present some other of the above functions.

6. Nineteen examples having trinitromethyl groups. These may have mononitro but no *gem*-dinitro functions.

7. Nine trinitromethyl compounds also containing *gem*-dinitro groups.

8. Five examples having *gem*-dinitro groups only.

9. Six nitroaromatics, five having polynitroaliphatic groups attached.

10. Seven fluorodinitromethyl compounds.

In all but category 4, examples are presented in which "dead-weight" carboxyl groups are present as well as examples in which they are absent. A plot of OB/100 vs impact sensitivity on a logarithmic scale for these compounds is given in Figure 1.

At first glance at Figure 1 in which no distinction is made between types of compounds shows the expected general increase in impact height with increasing OB/100. The band within which all compounds fall is quite broad with impacts ranging from 5 to 16 cm at OB/100 = + 3.0, from 11 to 72 cm at OB/100 = + 0.30 and from 34 to 220 cm at OB/100 = - 1.25. At equivalent impact heights, e.g. 32-34 cm, OB/100 varies from - 1.5 to + 1.7. Closer inspection of the plot, however, shows several areas of regularity.

Categories 1 - 5, Nitramines and Nitramides (●): Compounds in categories 1 - 5, which share the common property that each has at least one nitro group attached directly to nitrogen, almost uniformly fall at lower impact heights than the other polynitroaliphatics at equivalent values of OB/100. It appears, indeed, that the forty-five compounds in these five categories, represented by filled-in circles on the plot, show the hoped-for statistical distribution about a straight line which would describe a linear relationship between the logarithm of the impact height and OB/100.

Since it would be overly precise to attempt a least-squares treatment based on measurements as inexact as those obtained from the impact machine, we have by inspection delineated an area within which it is expected a least-squares line would fall and whose width at any impact height is equivalent to 10% of that height. This area, hereafter called the "true trend" for N-nitro compounds, may be described by the approximation

$$\log \text{I. S.} \pm 0.02 = 1.38 - (0.18)\,(\text{OB}/100)$$

where I. S. represents the 50% impact height.

Of the forty-five nitramino and nitramido compounds, fifteen fall in the area of the "true trend", an additional seventeen within 10% of the area and an additional seven within between 10 and 30% of the area. Of the other six, none was more than 80% off the value predicted by the "true trend." Since TNT, the standard for impact determinations, has shown impact values ranging from below 100 to above 250 cm, and considering that for a period of over three months impact sensitivities of TNT consistantly ran between 20 and 40% high, the distribution is as good as could be hoped for if the relationship claimed is truly a fact of nature.

An attempt was made to determine whether within the overall classification "N-nitro compounds" there was any preferred concentration of points above or below the "true trend" according to structure. The five individual categories comprising the group each show more-or-less random distribution as do categories based on the number of nitramino groups in the molecule or molecular weight. There is a slight tendency for compounds containing "dead weight" carboxyl groups to fall above the "true trend" and for primary nitramines to fall below.

Categories 6 and 7, Trinitromethyl Compounds (○): The twenty-eight compounds falling into these two classes, represented by empty circles in the plot, also distribute about a straight line relating the logarithm of impact sensitivity with OB/100. A "true trend" for polynitroaliphatic compounds based on these points is shown in Figure 1 and may be described by

$$\log \text{I. S.} \pm 0.02 = 1.76 - (0.22)\,(\text{OB}/100)$$

Of the twenty-eight compounds, eight fall in the area of the "true trend", an additional thirteen within 10%, four within between 10 and 30% and three within between 30 and 60%. Again, if the tendency for compounds containing "dead weight" carboxyl groups to fall above the "true trend" is real, it is only slight.

At OB/100 = + 2.0 this "true trend" predicts an impact height twice that of the N-nitro "true trend"; at OB/100 = - 2.0, impact heights are three times as great. The question of why polynitroaliphatics and N-nitro compounds follow separate trends will be discussed below, as will the suggestion that lower heats of formation and higher heats of detonation of N-nitro compounds cause lower impact heights at equivalent values of OB/100. It is meanwhile instructive to consider two pairs of compounds, structurally identical with the exception that in each case a nitramino group replaces a *gem*-dinitro. Tie-lines between the compounds considered are drawn in Figure 1.

No.	Compound ($X = NO_2$)	OB/100	Heat of Detonation Cal/g	Impact Sensitivity
66	$CH_3CX_2CH_2CX_2COOCH_2CX_3$	-0.28	1035	70
23	$CH_3NXCH_2CH_2COOCH_2CX_3$	-0.97	970	35
72	$CX_3CH_2OOCCH_2CH_2CX_2CH_2CH_2COOCH_2CX_3$	+0.35	1115	68
29	$CX_3CH_2OOCCH_2CH_2NXCH_2CH_2COOCH_2CX_3$	0.0	1065	29

In each instance the nitramino compound has a lower value of OB/100 and a lower calculated heat of detonation but it still much more sensitive.

Category 8, gem-Dinitro Compounds (△): Compounds 77 and 78 lie well above the "true trend" for polynitroaliphatic compounds while with compounds 74, 75 and 76 the points fall much lower. The last three share in common the fact that each has a gem-dinitro group in a position alpha or beta to another secondary nitro linkage and it may be that this is a sterically unfavorable situation as far as impact sensitivity is concerned. This seems borne out by the fact that compounds 65 and 73 of Category 7 which contain this structural feature also exhibit the same behavior.*

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* Another example is 2,2,4,4-tetranitropentanediol-1,5, OB/100 = + 1.41, which would be predicted to show I. S. = 28 cm if it followed the polynitroaliphatic trend. It actually shoots at less than half that height (3).

Category 9, Aromatic Compounds (□): Polynitroalkyl nitrobenzenes seem more sensitive than polynitroaliphatics at equivalent values of OB/100, viz., Compounds 80, 83, and trinitroethyl p-nitrobenzene (I. S. = 20 cm, OB/100 = - 2.09). No generalization seems possible for polynitroalkyl polynitrobenzoates on the basis of the limited number of cases studied.

Category 10, Fluorodinitro Compounds (■): A detailed evaluation of this interesting new class of compounds will be presented in a separate report(1). It can be seen from the plot that as a class they appear quite promising.

COMPARISON WITH PERFORMANCE PARAMETERS

It has been suggested that impact heights might show a similar relationship with some experimentally determinable measure of explosive performance such as heat of detonation. For this to be the case OB/100 would, in turn, show a regular variation with the same parameter.

In a separate report (4) heats of detonation have been plotted as a function of OB/100 for a series of structurally related linear nitramines*. The plot showed the expected maximum at OB/100 = + 2.5, the carbon dioxide level, with additional oxidant above this level acting only as a diluent. In addition, however, there was observed a minimum at OB/100 = zero and a second maximum at OB/100 = ca - 5.5, the hydrogen level**. The reason for this unexpected behavior as OB/100 went below zero was that water, $\Delta H_f = 57.8$ Kcal/mole, was formed as a detonation product in preference to and at the expense of carbon monoxide, $\Delta H_f = 26.4$ Kcal/mole.

Comparing Figure 1 with the Heat of Detonation vs. OB/100 plot (4) the behavior may be summarized as follows:

Increasing OB/100	Heat of Detonation	50% Impact Height
<- 5.5 to - 5.5	increases	decreases
- 5.5 to 0	decreases	decreases
0 to + 2.5	increases	decreases
+ 2.5 to >+ 2.5	decreases	decreases

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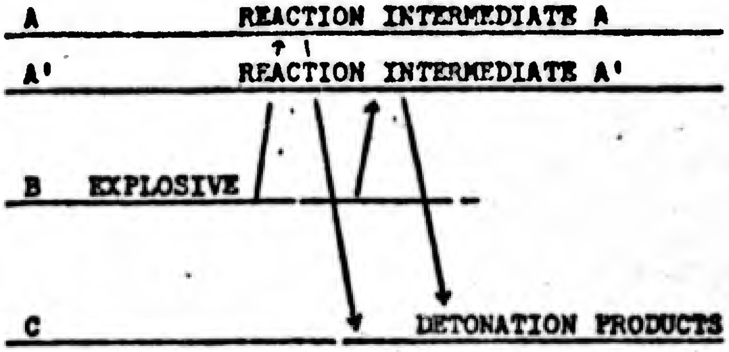
* Heats of detonation were calculated using the Brinkley-Wilson convention that all hydrogen is burned to water before carbon is burned to carbon monoxide (5).

** It is believed that this is a new term. The hydrogen level may be defined as that at which there is sufficient oxygen to burn all the hydrogen but none of the carbon.

as a consequence of this and of the differing trends for different classes of compounds, a plot of logarithmic impact sensitivity as a function of heat of detonation shows an apparently random distribution of points (Figure 2, data in Table II). For similar classes of compounds over limited ranges of OB/100 there may be regular behavior, viz., linear nitramines in the ranges OB/100 = + 2.5 to OB/100 = 0 (solid line) and OB/100 = 0 to OB/100 = - 5.5 (broken line). Even over these short ranges, however, the regularity of the behavior disappears when the heat of formation of the compound differs substantially from those of others in the series, e.g., Tetryl, compound XII

On considering on a molecular scale what happens under the impact hammer, there seems adequate reason for the absence of any simple direct correlation between heat of detonation and impact sensitivity. Wenograd (6) has demonstrated a linear relationship between logarithmic impact heights of a number of high explosives and k_{500}, their thermal decomposition rates extrapolated to 500°C, Bowden's estimate of the "hot-spot" temperature (7). A strong case can be made that the rate determining step in thermal decompositions is the first thermal cleavage of a bond in the previously intact molecule. Kinetic theory requires that the first bond broken be the weakest bond in that molecule. It would follow that the amount of energy required to break that bond would be the activation energy in the decomposition process and would be a factor strongly influencing impact sensitivity. This seems to be borne out by the clustering in Figure 1 around a separate lower trend for compounds containing N-nitro linkage as compared with polynitroaliphatic compounds containing only C-nitro linkages. The N-nitro bond, being much weaker than the C-nitro bond is almost certainly the one more readily broken.

The heat of detonation, on the other hand, depends only on the difference in energy between the explosive and its decomposition products and is independent of the route taken in the process. It is not a function of the strength of any single bond broken in any single step, but is an aggregate function of all bonds broken and all bonds formed in all steps. Schematically, the situation may be shown as follows:



For a decomposition in which the breaking of the first bond generates intermediate A, the distance B-A would be the activation energy, an endothermic quantity strongly influencing both impact sensitivity and rate. The distance A-C represents the exotherm in subsequent steps and the distance B-C, which is the sum of endotherm and exotherm, is a measure of the heat of detonation. Had this decomposition gone through intermediate A', we would have the same exothermic result, B-C, but a different endothermic process, B-A' influencing both rate and impact sensitivity. The statement that there is no relationship between heat of detonation and impact sensitivity is therefore tantamount to saying that you can't tell the height of a mountain from the difference in altitudes of the valleys on either side.

It will be noted that in the above argument we have stated that on a molecular scale the amount of energy required to break the weakest bond is "a factor strongly influencing impact sensitivity" rather than "the sole factor determining impact sensitivity." The latter would be true if on a macro scale the question of whether or not a compound shot at a given height depended on the initiation phenomenon alone. This does appear to be the case with RDX as evidenced by the fact that there is generally a strong "go" or all "no-go" distinction with variation of drop height on the machine. If the ignition process starts, it goes far enough to register as a positive result.

With certain classes of compounds, however, there is a greater tendency to show "partials" at many heights (8), i.e., the decomposition process starts but may or may not die off before enough energy is liberated as sound to trigger the sensing mechanism. In such instances the propagation step may also be a factor influencing impact sensitivity. As before, such cases would on a molecular scale depend strongly on the amount of energy required to break the weakest bond, but would also depend to an extent on the amount of energy made available to a molecule by the decomposition of a neighboring molecule. The latter quantity shows at least partial dependence on the heat of detonation.

MECHANISM

Having shown why impact sensitivity does not depend mainly on heat of detonation, it remains only to postulate why it should depend on OB/100. The above argument requires that there be some relationship between OB/100 and the ease of breaking of the weakest bond.

With compounds containing only C-nitro bonds, the rationalization is easy. OB/100 is roughly a function of the number of nitro groups in the molecule. The more C-nitro bonds and the fewer C-C, C-H and C-O bonds in a molecule, the greater is the probability that of the total molecular energy sufficient will be localized in a C-nitro bond to cause its rupture. In kinetic terms this would manifest itself as an increasing entropy of activation with increasing OB/100*.

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*Another way of looking at it is as an increasing pre-exponential factor in the Arrhenius equation.

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With compounds containing at least one N-nitro bond, however, the plot in Figure 1 seems to show that no matter how many C-nitro linkages are added, the N-nitro is the bond broken. Increased entropy of activation would furnish no explanation here.

Pauling has shown that the strength of a given bond X-Y is a function of contributions from resonance structures of the type

$$\underset{\text{I}}{X-Y} \qquad \underset{\text{II}}{X^+ \; Y^-} \qquad \underset{\text{III}}{X^- \; Y^+}$$

The greater the difference in the electronegativities of X and Y, the greater is the contribution from resonance structures such as II and III and the greater is the strength of the bond (9). For this reason the H-F bond is very much stronger than either the H-H bond or the F-F bond. With nitramines the corresponding resonance structures are

$$\underset{\text{IV}}{N-NO} \qquad \underset{\text{V}}{N^+ \; NO_2^-} \qquad \underset{\text{VI}}{N^- \; NO_2^+}$$

and there is in addition the double bonded resonance structure

$$\underset{\text{VII}}{\overset{+}{N}=NO_2^-}$$

Of these, IV, V and VII are the greatest contributors, VI is minor. The importance of such a resonance contributor as VII is evidenced by the partial double bond character with shortening of the N-N bond in nitramines, EDNA showing an N-N bond distance of 1.33 Å as compared to 1.45Å for dimethylhydrazine (10).

The argument to be made here is that with increasing OB/100 we have increasing numbers of electron withdrawing groupings exercising an increasing inductive electron withdrawal effect on the nitrogen atom to which the nitro group is attached. The effect is a cumulative decrease in the difference in electronegativities between the two adjoining nitrogen atoms and in the energy of such resonance structures as V and VII. This, leading in turn to a cumulative decrease in the contribution of these resonance structures to the overall strength of the bond, results in a progressively lower activation energy with progressively increasing OB/100.

The above is not to be construed as more than an extreme simplification of what is probably quite a complex process. Wenograd's linear correlation between logarithmic impact sensitivity and k_{500} has been mentioned (6). He has also tabulated activation energies and pre-logarithmic factors for the reactions considered. There was no simple correlation between either of these quantities and impact heights. Nor is it the case here that changes in either activation energy or entropy alone influence sensitivity depending on the class of compounds. Any correlation will necessarily involve a complex function incorporating varying contributions from both and is beyond the scope of our present knowledge of decomposition kinetics.

A well-planned kinetic study might tell us more about the detailed mechanism of impact sensitivity on a molecular scale. This would involve the thermal decomposition in solution of several series of structurally related compounds with regularly varying values of OB/100.

TWO-COMPONENT MIXTURES

In considering the sensitivity of pure compounds one has to contend only with the vagaries of the impact machine. With more than one component there is the additional complication that the method of mixing is also suspect. One never knows whether the 35 mg sample taken for the individual shot fairly represents the overall composition of the aggregate. Unfortunately, such phenomena as segregation and clustering appear to be the rule rather than the exception.

Since systemic errors in multi-component systems are more to be expected than with single compounds, we have been more selective in the choice of examples for consideration. We have confined ourselves to pairs for which large numbers of measurements are available and for which results taken over a span of years by a number of workers show a measure of agreement. The data have, as before, been taken from the periodic NAVORD reports of the Explosives Properties Division covering the interval 1 January 1950 to 1 November 1956 (2).

Explosive plus Explosive: Plots of logarithmic 50% impact heights as functions of OB/100 are shown in Figure 3 for mixtures of RDX with TNT and with bis-dinitropropyl fumarate (DNPF). In both cases the points distribute about straight lines connecting the logarithmic impact heights of the individual components. Probably the most reliable of the points on the plot is that for Composition B at OB/100 = - 1.50. Although not strictly a two-component system since it contains 1% wax, it seems significant that the accepted impact sensitivity of 60-65 cm agrees well with the 62 cm predicted if

Based on an average of tens of thousands of shots, Composition A (91% RDX-9% wax) has an impact sensitivity of 70-75 cm. OB/100 for this mixture is -2.58*. At an equivalent value of OB/100 a pure explosive, if it followed the "true trend" for N-nitro compounds, would be predicted to have an impact sensitivity of 67-73 cm.

Additional data for this and other proportions of RDX and Stanolind wax** are plotted in Figure 5. It can be seen that for compositions ranging from 2 to 15% wax there is an approximately equal distribution of points above and below the "true trend" (solid line).

Also plotted in Figure 5 are data for TNETB - Stanolind wax mixtures at compositions from 1 to 15% wax together with the "true trend" for polynitroaliphatic compounds. Here it appears that if a least-squares line should be drawn through these points the line would closely parallel the "true trend" for this class of compounds.

Shown schematically below are the types of behavior which might result on addition of wax to explosive.

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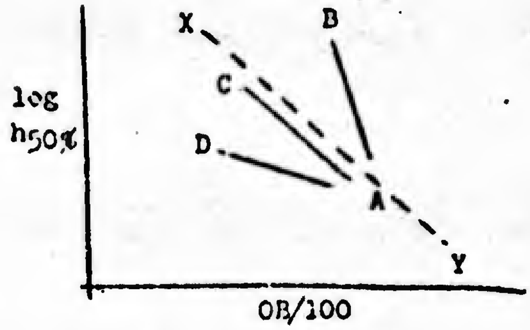
*In the calculations waxes are considered to be mainly polymethylene, OB/100 = -28.6.

** Of the mass of available data for the many waxes tried, that for Stanolind wax seems the most self-consistent. Considering that the scatter of points in Figure 5 is what we call self-consistency, it can be imagined how the points for the other waxes scatter.



If the point A represents an explosive compound and the broken line X-Y the "true trend" of the class into which that compound falls, the arrow A-C describes the behavior of both RDX and TNETB on addition of wax. This effect is one of dilution, not desensitization. The same result was obtained on adding methylene groups in the form of a wax coating on the explosive crystal as would be predicted had the same quantity of methylene groups been incorporated within the structure of the molecule.

True desensitization would imply the behavior described by the arrow A-B. The decrease in sensitivity on coating crystal surfaces with wax would be greater than that anticipated simply by dilution. Many cases of A-B behavior have been reported, but none has ever been reproduced and it appears that in conventional "desensitization" it has never truly occurred. If it had, the composition would probably now be in service use.

Behavior described by the arrow A-D has also often been reported. It is a necessary consequence of segregation that if A-C represents ideal behavior and if one portion of a mixture follows A-B behavior, another portion will follow A-D.

It is our belief that the impact sensitivity of an explosive on "desensitization" approaches that anticipated on dilution as mixing and sampling approach ideality. While the validity of all other evidence is suspect, the value for Composition A seems unassailable and strongly supports this belief.

CONCLUSIONS, COMMENTS AND RECOMMENDATIONS

A number of conclusions may be drawn from this study and from the accompanying report (4). If correct they support recommendations on future research and development in the field of explosive chemistry.

(1) Nitramines are more sensitive than other polynitroaliphatic compounds at equivalent values of OB/100 and at equivalent heats of detonation. The N-nitro linkage appears to be a built-in sensitizing group. It is perhaps unfortunate that of the three compounds most commonly used in explosive chemistry, RDX, tetryl and TNT, two are of this class. In the further synthesis of new high explosives and propellants, the N-nitro linkage should be avoided. Conversely. at every value of OB/100, polynitroaliphatic compounds not containing the N-nitro linkage are less sensitive than pure explosives and explosive compositions now in use.

(2) For N-nitro compounds and for polynitroaliphatics as separate classes, there are linear relationships between logarithmic impact heights and OB/100. These relationships have a number of potential uses.

(2-a)One can predict the sensitivity of a compound prior to making it. This furnishes a preliminary indication of how the compound should be handled.

(2-b)One can determine whether within a class additional structural features tend to sensitize or desensitize. Fluorodinitromethyl compounds, for example, appear quite promising as a group because their impact sensitivities generally fall above the "true trend" for polynitroaliphatics. Conversely, compounds with the *gem*-dinitro linkage *alpha* or *beta* to a secondary nitro group appear not to be promising because impacts fall well below the "true trend."

(2-c)Individual compounds may be evaluated. *bis*-Trinitroethyl 4,4-dinitropimelate (Compound 72) shoots at 65 cm whereas its impact height is predicted to be 50 cm. If on a 1000-shot determination this result should be repeated, the compound might be worth further consideration Other properties of this compound are of interest since it will be mentioned again.

m.p., 171°
Impact Sensitivity, 68 cm; $\sigma = 0.02$
Crystal Density, 1.71 g/cm ^{3}
Thermal Stability, 0.18 cc/g/24 hr.
Ignition Temperature 221°
Calculated Heat of Detonation, 1115 Cal/g

Among high-oxygen high explosives, the 50% impact height of BTNEC, 16 cm, is substantially above the value predicted, 9-10 cm. Sufficient determinations have been made to indicate that 16 cm is a reliable value. It would follow that for applications in which high oxygen content is required BTNEC should be used in preference to TNETB, BTNEU, BTNEN or TNEOC, all of which fall within or below the "true trend."

(3) Compounds balanced to, or close to, the hydrogen level have calculated heats of detonation as great or greater then RDX, but are very much less sensitive to impact. This is a consequence of the fact that calculated heats of detonation increase on going from OB/100 = 0 to OB/100 = -5.5 while sensitivities decrease. Such compounds should be synthesized and evaluated for self-explosive applications. Compounds balanced at or close to the carbon monoxide level are comparatively inefficient as self-explosives.

(4) If mixing is ideal, a plot of logarithmic impact heights of mixtures of explosive plus explosive as a function of OB/100 should show points distributing about a straight line connecting the impact heights of the individual components. Such a plot may serve to tell how effective a mixing procedure is.

(5) With ideal mixing the impact sensitivity of explosive plus wax is that predicted at an equivalent value of OB/100 by the "true trend" of the class into which that explosive falls. Conventional "desensitization" appears merely to be a process of dilution. If this be the case, why "desensitize?" The same result may be achieved by incorporating the same quantity of methylene groups within the structure of the explosive molecule, i.e., "tailor-making" a molecule with the same value of OB/100 as explosive plus wax. A number of advantages result.

Problems of segregation, stratification, preferential exudation, sampling, etc. are eliminated. Batch to batch reproducibility is much easier. In "desensitizing" RDX we must build around the physical characteristics of this compound; in tailor-making we can choose between many possible sets of physical properties. A wide variety of compounds is potentially available at any value of OB/100 desired. A comparison worth making is the following:

	RDX	Comp. A	bis-Dinitrobutyl nitramine (11)
OB/100	0	-2.58	-2.82
Impact Sensitivity, cm	23.9	70-75	80
m.p.	205°(d)	ca 185°(d)	106-7°
Crystal Density, g/cm ^{3}	1.81	1.70-1.73	1.71
Calc'd. Heat of Detonation, cal/g	1230	1200	1225

(6) With polynitroaliphatics the "true trend" shows what can best be hoped for as far as the sensitivity of pure compounds is concerned. A continuing attempt in the synthesis program has been to synthesize molecules with higher and higher oxygen balances within this class. After making these compounds we generally have to "desensitize" them to sensitivities of 60-70 cm prior to use. If the "desensitization" is ideally a process of dilution, should we not within this class be satisfied with the best pure compound available in the 60-70 cm range (possibly bis-trinitroethyl 4,4-dinitropimelate) and discontinue attempts at further synthesis of high-oxygen compounds.

This should not be implied as meaning that the entire high-oxygen synthesis program should be discontinued. We should look for new classes of compounds or new desensitizing structural features. The impact sensitivities of the fluorodinitro compounds, for example, indicate that these may fall into a separate "true trend" with better oxidant balances at all impact heights. Other new classes of compounds may act similarly.

NOTE WELL: In recommending against "desensitization" we confine ourselves to the conventional method of coating explosive crystals with wax. Work currently being done on desensitization by solution is promising and may offset many of the arguments made here.

ACKNOWLEDGMENT

This study had its nascence in a series of discussions with Dr. Darrell V. Sickman. The mechanism section is a distillate of four years of arguments, agreements, postulates and proposals. The author is grateful for both impetus and stimulus. Thanks are also due to Drs. Hans Snay, Donna Price, Sigmund Jacobs, O. H. Johnson and J. M. Rosen for advice and information; to H. Heller and especially Mrs. Sarah Duck for their cheerful cooperation in assembling the impact results.

TABLE I

IMPACT SENSITIVITY AND OB/100 OF SELECTED EXPLOSIVES

No.	Compound Name	Mol. Formula	M.W.	O.B.	OB/100	I.S.
	1. Nitramines					
1	MEDINA	$CH_4N_4O_4$	136	+ 2	+1.47	13
2	EDNA	$C_2H_6N_4O_4$	150	- 2	-1.33	34
3	RDX	$C_3H_6N_6O_6$	222	0	0	24
4	N-methyl EDNA	$C_3H_8N_4O_4$	164	- 6	-3.65	114
5	HMX	$C_4H_8N_8O_8$	296	0	0	26
6	3-nitraza-1,5-pentanedinitramine	$C_4H_{10}N_6O_6$	238	- 6	-2.52	36
7	3,6-dinitraza-1,8-octanedinitramine	$C_6H_{14}N_8O_8$	326	-10	-3.07	33
8	Tetryl	$C_7H_5N_5O_8$	287	- 3	-1.04	32
	2. Nitramine plus gem-Dinitro					
9	3,3-dinitropentanedinitramine	$C_5H_{10}N_6O_8$	282	- 4	-1.42	35
10	N,3,3,5,5-pentanitropiperidine	$C_5H_6N_6O_{10}$	310	+ 4	+1.29	14
11	bis-dinitropropylnitramine	$C_6H_{10}N_6O_{10}$	326	- 2	-0.61	29
12	bis-dinitrobutylnitramine	$C_8H_{14}N_6O_{10}$	354	-10	-2.82	60
13	2,2,4,7,9,9-hexanitro-4,7-diazadecane	$C_8H_{14}N_8O_{12}$	414	- 6	-1.45	72
14	2,2,4,7,7,10,12,12-octanitro-4,7-diazatridecane	$C_{11}H_{18}N_{10}O_{16}$	546	- 8	-1.47	44
15	2,2,5,7,7,9,12,12-octanitro-4,7-diazatridecane	$C_{11}H_{18}N_{10}O_{16}$	546	- 8	-1.47	37
	3. Nitramine plus Trinitromethyl					
16	methyl trinitroethylnitramine	$C_3H_5N_5O_8$	239	+ 5	+2.09	9
17	BTNEN	$C_4H_4N_8O_{14}$	388	+16	+4.12	5
18	trinitroethyl trinitropropylnitramine	$C_5H_6N_8O_{14}$	402	+12	+2.98	6
19	N,N'-bis-trinitroethyl MEDINA	$C_5H_6N_{10}O_{16}$	462	+16	+3.46	5
20	N-methyl-N'-trinitroethyl EDNA	$C_5H_9N_7O_{10}$	327	+ 1	+0.30	11
21	trinitroethyl N-trinitroethylnitraminoacetate	$C_6H_6N_8O_{16}$	446	+12	+2.69	9
23	trinitroethyl 4-nitrazavalerate	$C_6H_9N_5O_{10}$	311	- 3	-0.97	35
24	trinitroethyl 3,3-dinitrobutylnitramine	$C_6H_9N_7O_{12}$	371	+ 3	+0.81	20
25	bis-trinitroethyl 3-nitrazaglutarate	$C_8H_8N_8O_{18}$	504	+ 6	+1.58	14
26	1,1,1,3,6,9,11,11,11-nonanitro-3,6,9-triazaundecane	$C_8H_{12}N_{12}O_{18}$	564	+ 8	+1.42	12
27	1,1,1,3,6,6,9,11,11,11,-decanitro-3,9-diazaundecane	$C_9H_{12}N_{12}O_{20}$	608	+10	+1.64	10
28	1,1,1,4,6,6,8,11,11,11-decanitro-4,8-diazaundecane	$C_9H_{12}N_{12}O_{20}$	608	+10	+1.64	11
29	bis-trinitroethyl 4-nitrazaheptandioate	$C_{10}H_{12}N_8O_{18}$	532	0	0	25
30	1,1,1,3,6,9,12,14,14,14-decanitro-3,6,9,12-tetrazatetradecane	$C_{10}H_{16}N_{14}O_{20}$	652	+ 4	+0.61	19
31	bis-trinitroethyl 3,6-dinitraza-1,8-octandioate	$C_{10}H_{12}N_{10}O_{20}$	592	+ 4	+0.67	29
32	1,1,1,3,6,6,8,10,10,13,15,15,15-tridecanitro-3,8,13-triazapentadecane	$C_{12}H_{16}N_{16}O_{26}$	800	+12	+1.50	23

TABLE I (Cont'd.)

No.	Compound Name	Mol. Formula	M.W.	O.B.	OB/100	I.S.
	4. Nitramine plus Nitrate Ester					
33	trinitroethylnitraminoethyl nitrate	$C_4H_6N_6O_{11}$	314	+10	+3.19	7
34	trinitroethylnitraminopropyl nitrate	$C_5H_8N_6O_{11}$	328	+ 6	+1.83	12
35	3,5,5-trinitro-3-azahexyl nitrate	$C_5H_9N_5O_9$	283	- 1	-0.35	21
	5. Nitramides					
36	N-nitro-N-trinitropropyl trinitroethyl carbamate	$C_6H_6N_8O_{16}$	446	+12	+2.70	9
37	trinitroethyl 2,5-dinitrazahexanoate	$C_6H_9N_7O_{12}$	371	+ 1	+0.27	15
38	trinitroethyl 2,5,5-trinitro-2-azahexanoate	$C_7H_9N_7O_{14}$	415	+ 3	+0.72	22
39	trinitroethyl 2,4,6,6-tetranitro-2,4-diazaheptanoate	$C_7H_9N_9O_{16}$	475	+ 7	+1.47	13
40	N,N'-dinitro-N,N'-bis-(trinitropropyl)-oxamide	$C_8H_8N_{10}O_{18}$	532	+12	+2.26	9
41	2,2,6,9,9-pentanitro-4-oxa-5-keto-6-azadecane	$C_8H_{12}N_6O_{12}$	384	- 6	-1.56	47
42	1,1,1,5,7,10,14,14,14-nonanitro-3,12-dioxa-4,11-diketo-5,7,10-triazatetradecane	$C_9H_{10}N_{12}O_{22}$	638	+12	+1.88	11
43	N,N'-dinitro-N,N'-bis-(3,3-dinitrobutyl)-oxamide	$C_{10}H_{14}N_8O_{14}$	470	- 6	-1.28	37
44	1,1,1,5,8,11,14,18,18,18-decanitro-3,16-dioxa-4,15-diketo-5,8,11,14-tetrazaoctadecane	$C_{12}H_{16}N_{14}O_{24}$	740	+ 4	+0.54	19
45	N, N'-dinitro-N,N'-bis-(3-nitrazabutyl)-oxamide	$C_8H_{14}N_8O_{10}$	382	-10	-2.61	90
	6. Trinitromethyl Compounds					
46	trinitroethylcarbamate	$C_3H_4N_4O_8$	224	+ 4	+1.79	18
47	methyl trinitroethyl carbonate	$C_4H_5N_3O_9$	239	+ 3	+1.25	28
48	1,1,1,3-tetranitropropane	$C_4H_4N_4O_8$	236	+ 4	+1.70	33
49	methylene-bis-trinitroacetamide	$C_5H_4N_8O_{14}$	400	+14	+3.50	9
50	heptanitropentane	$C_5H_5N_7O_{14}$	387	+13	+3.36	12
51	BTNEC	$C_5H_4N_6O_{15}$	388	+14	+3.60	16
52	BTNEU	$C_5H_6N_8O_{13}$	386	+10	+2.60	17
53	5,5,5-trinitropentanone-2	$C_5H_7N_3O_7$	221	- 3	-1.36	125
54	TNETB	$C_6H_6N_6O_{14}$	386	+ 8	+2.07	18
55	ethyl trinitroethyl carbonate	$C_5H_7N_3O_9$	253	- 1	-0.39	81
56	trinitroethyl orthoformate	$C_7H_7N_9O_{21}$	553	+21	+3.80	7
57	1,1,1,7,7,7-hexanitroheptanone-4	$C_7H_8N_6O_{13}$	384	+ 4	+1.04	34
58	nitroisobutyl trinitrobutyrate	$C_8H_{12}N_4O_{10}$	324	-10	-3.09	279
59	trinitrobutyric anhydride	$C_8H_8N_6O_{15}$	428	+ 4	+0.93	30
60	N,N'-bis-trinitropropyloxamide	$C_8H_{10}N_8O_{14}$	442	+ 2	+0.45	45
61	bis-trinitroethylsuccinate	$C_8H_8N_6O_{16}$	444	+ 4	+0.90	30
62	TNEOC	$C_9H_8N_{12}O_{28}$	732	+28	+3.83	7
63	methylene-bis-trinitrobutyramide	$C_9H_{12}N_8O_{14}$	456	- 2	-0.44	113
64	ethylene-bis-trinitrobutyrate	$C_{10}H_{10}N_6O_{14}$	470	- 2	-0.43	120

TABLE I (Cont'd.)

No.	Compound Name	Mol. Formula	M.W.	O.B.	OB/100	I.S.
	7. Trinitromethyl plus gem-Dinitro					
65	N-trinitroethyl-3,3,5,5-tetranitropiperidine	[illegible]	425	+ 6	+1.40	18
66	trinitroethyl dinitrovalerate	[illegible]	355	- 1	-0.28	70
67	dinitropropyl trinitrobutyramide	[illegible]	354	- 2	-0.57	72
68	dinitrobutyl trinitrobutyrate	[illegible]	369	- 5	-1.35	101
69	trinitroethyl dinitrohexanoate	[illegible]	368	- 5	-1.35	138
70	N,N'-bis-dinitropropyl trinitrobutyramide	[illegible]	456	- 4	-0.82	72
71	dinitropropandiol bis-trinitrobutyrate	[illegible]	576	+ 2	+0.35	50
72	bis-trinitroethyl 4,4-dinitrohepandioate	[illegible]	576	+ 2	+0.35	68
73	bis-trinitroethyl 4,4,6,6,8,8-hexanitroundecanadioate	[illegible]	812	+ 6	+0.74	32
	8. gem-Dinitro Compounds					
74	3,3,4,4-tetranitrohexane	$C_6H_{10}N_4O_8$	266	- 6	-2.25	80
75	2,2,4,4,6-pentanitroheptane	[illegible]	325	- 5	-1.54	56
76	2,2,4,4,6,6-hexanitroheptane	[illegible]	370	0	0	29
77	bis-dinitropropyl oxalate	[illegible]	354	- 6	-1.70	227
78	dinitropropyl dinitrovalerate	[illegible]	324	-10	-3.09	320
	9. Aromatic Compounds					
79	TNT	$C_7H_5N_3O_6$	227	- 7	-3.08	160
80	trinitroethyl trinitrobenzene	[illegible]	376	+ 4	+1.07	13
81	trinitroethyl trinitrobenzoate	[illegible]	420	+ 4	+0.95	24
82	trinitroethyl 3,5-dinitrobenzoate	[illegible]	375	- 1	-0.27	73
83	trinitropropyl trinitrobenzene	[illegible]	390	0	0	20
84	dinitropropyl trinitrobenzoate	[illegible]	389	- 5	-1.29	214
	10. Fluorodinitro Compounds					
85	fluorodinitrobutyric Acid	[illegible]	196	- 2	-1.02	320
86	fluorodinitroethyl trinitrobutyrate	[illegible]	357	+ 5	+1.40	19
87	trinitroethyl fluorodinitrobutyrate	[illegible]	357	+ 5	+1.40	13
88	fluorodinitroethyl fluorodinitrobutyrate	[illegible]	332	+ 2	+0.66	52
89	fluorodinitroethyl 3,5-dinitrobenzoate	[illegible]	348	- 4	-1.15	140
90	tetrakis-(fluorodinitroethyl)-orthocarbonate	[illegible]	624	+16	+2.56	31,21
91	bis-fluorodinitroethyl carbonate	[illegible]	334	+ 8	+2.39	42

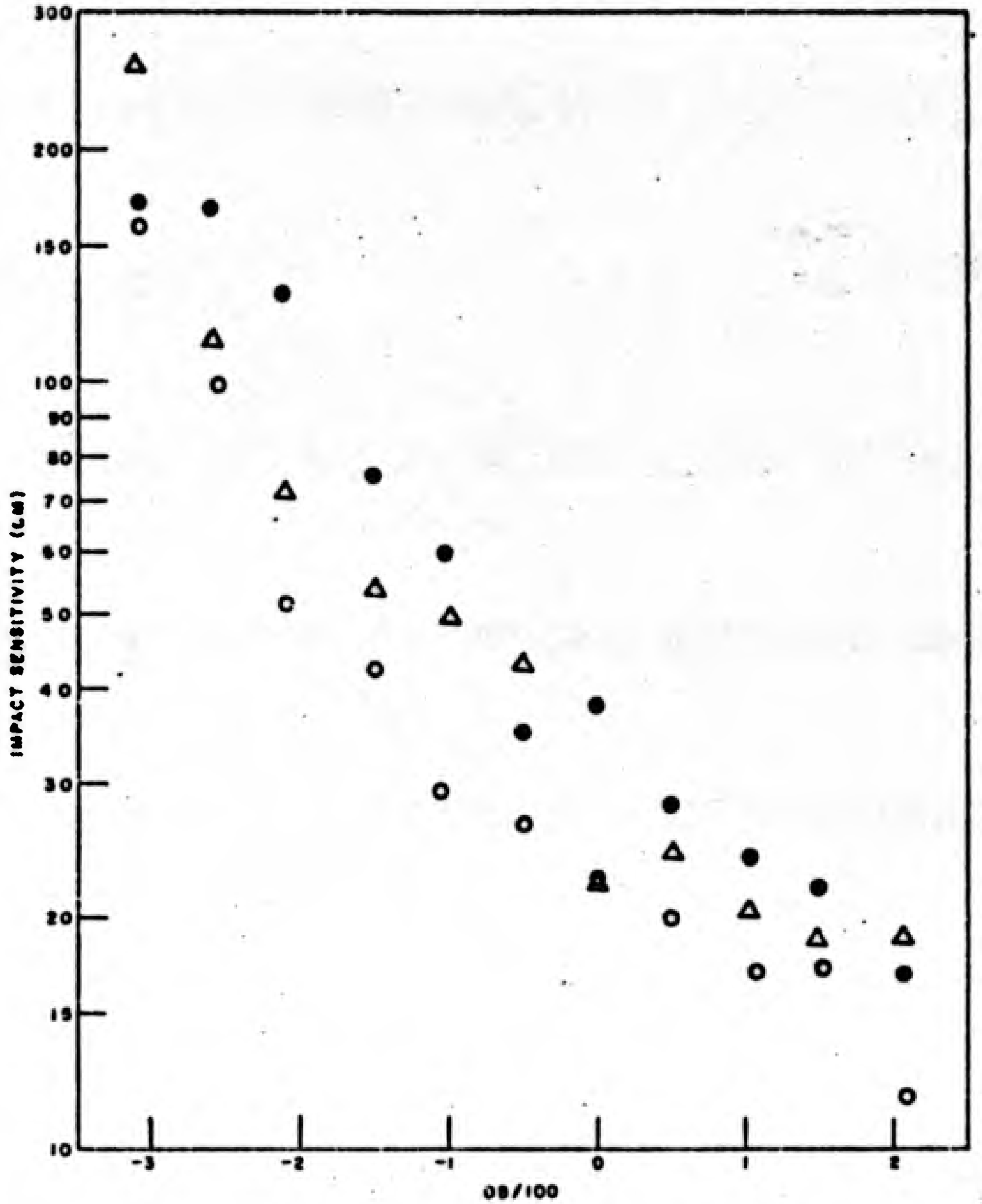


FIG. 4 IMPACT SENSITIVITIES OF TNETB-TNT MIXTURES AS FUNCTION OF OB/100

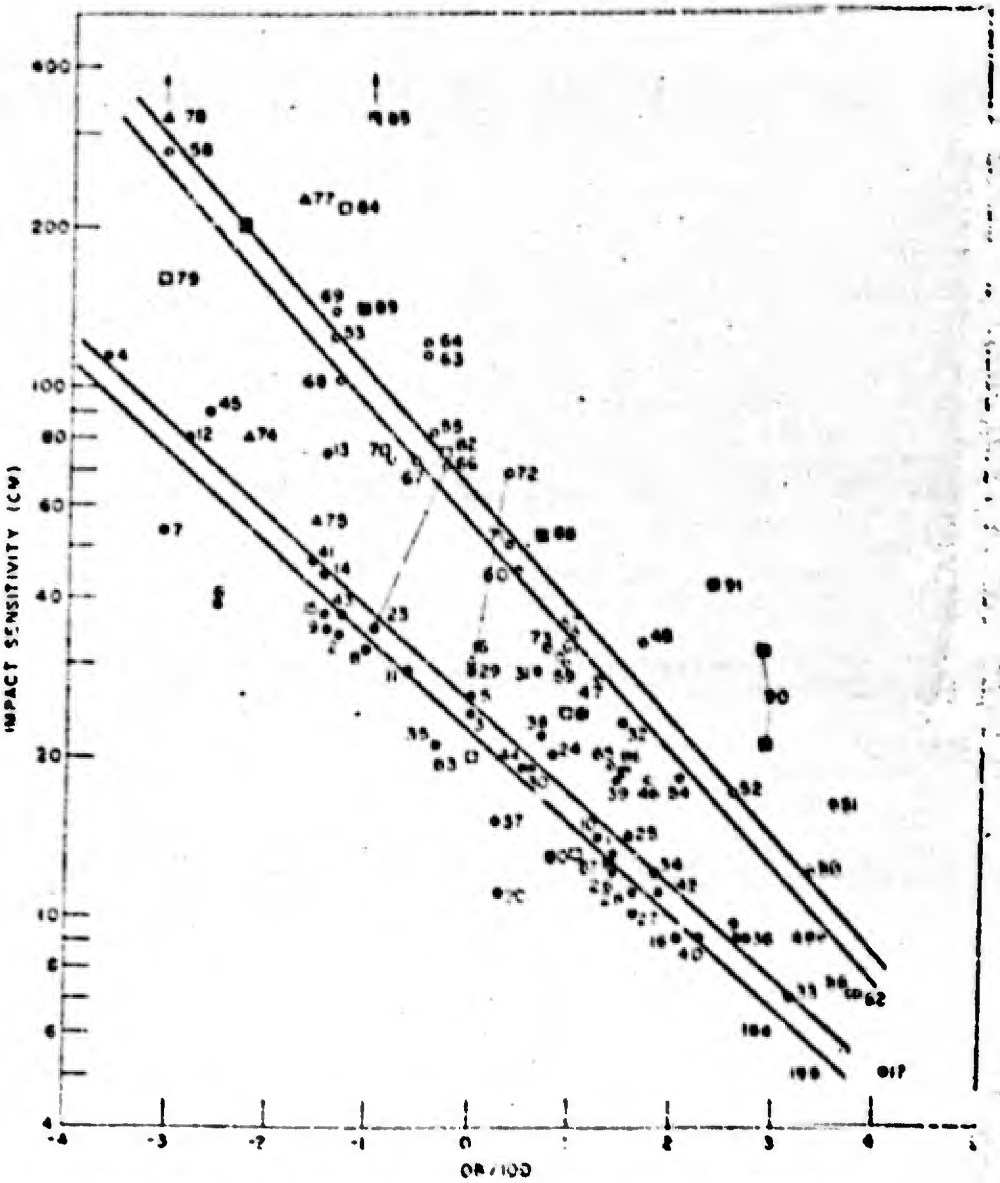
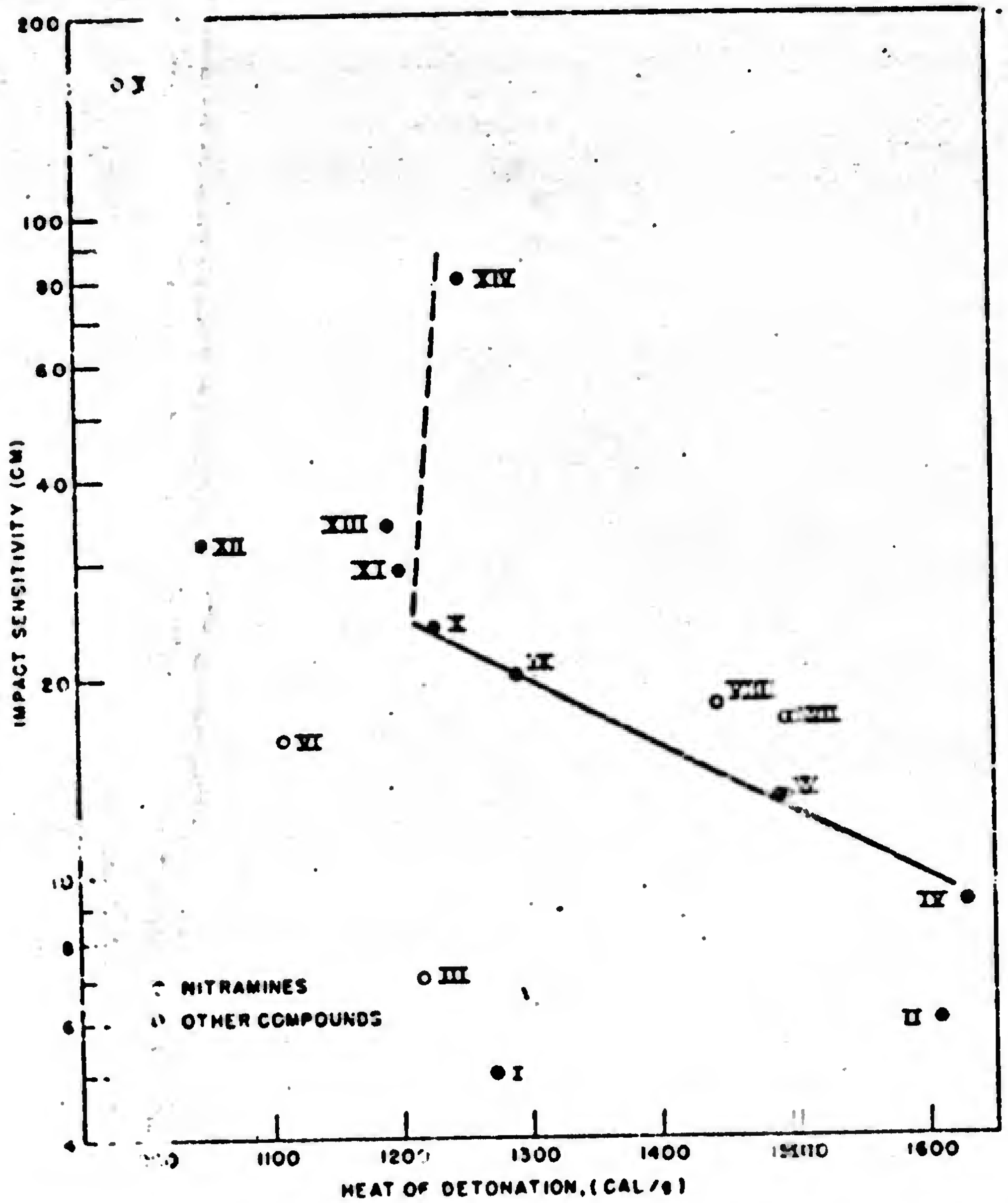


FIG. 1 IMPACT SENSITIVITY AS A FUNCTION OF OB/100

TABLE II

IMPACT SENSITIVITY AND HEAT OF DETONATION OF SELECTED EXPLOSIVES

No.	Compound	Impact Sensitivity, Cm.	Heat of Detonation, Cal./g
I	BTNEN	5	1270
II	trinitroethyl trinitropropyl nitramine	6	1610
III	TNEOC	7	1217
IV	methyl trinitroethyl nitramine	9	1630
V	MEDINA	13	1493
VI	BTNEC	15	1109
VII	BTNEU	17	1498
VIII	TNETB	18	1446
IX	trinitroethyl dinitrobutyl nitramine	20	1290
X	RDX	23.9	1220
XI	bis-dinitropropyl nitramine	29	1200
XII	Tetryl	32	1047
XIII	EDNA	34	1193
XIV	bis-dinitrobutyl nitramine	80	1250
XV	TNT	160	98



G 2 IMPACT SENSITIVITY AS A FUNCTION OF HEAT OF DETONATION

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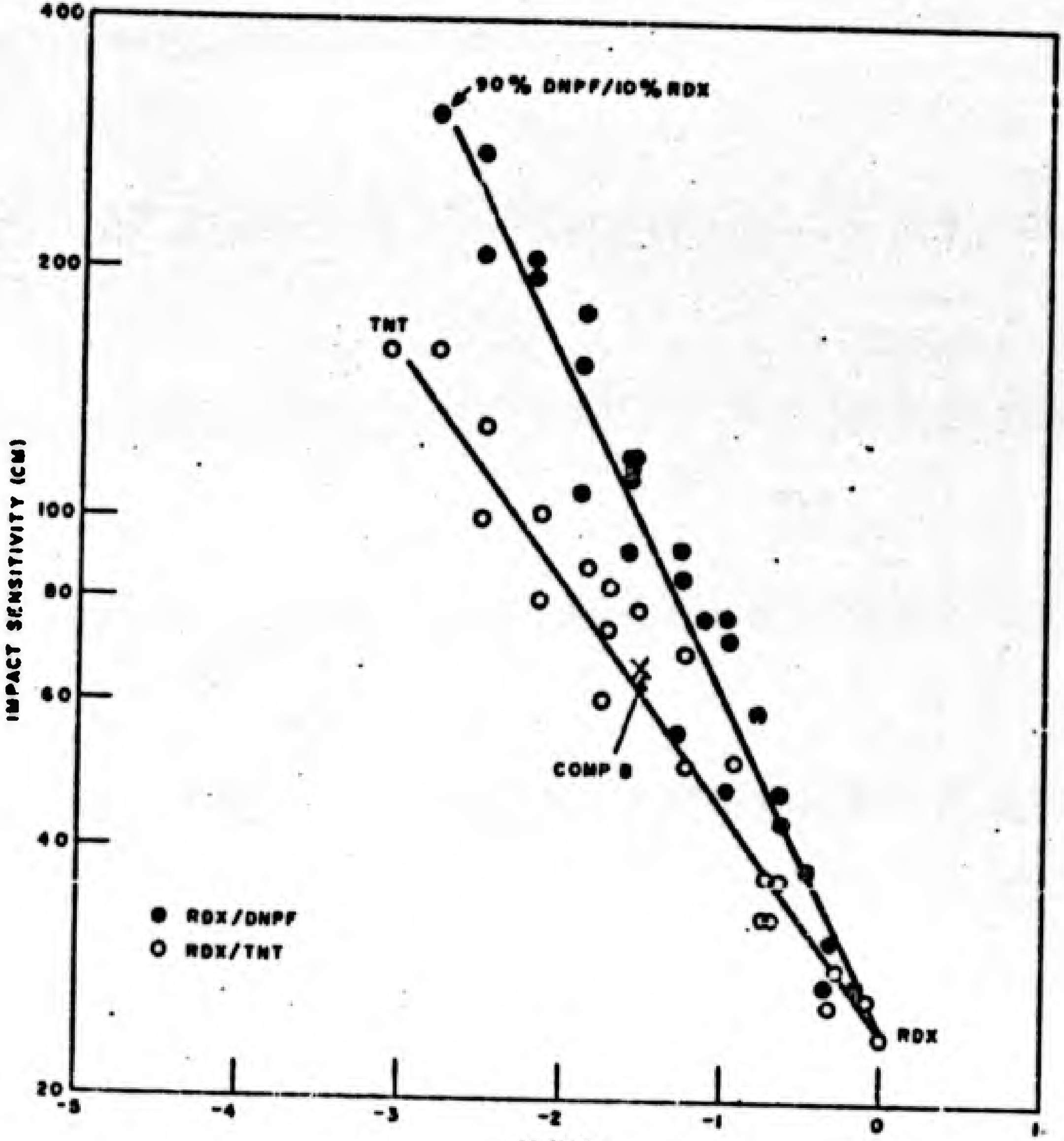

FIG. 3 IMPACT SENSITIVITIES OF RDX-TNT AND RDX-DNPF MIXTURES AS FUNCTIONS OF OB/100

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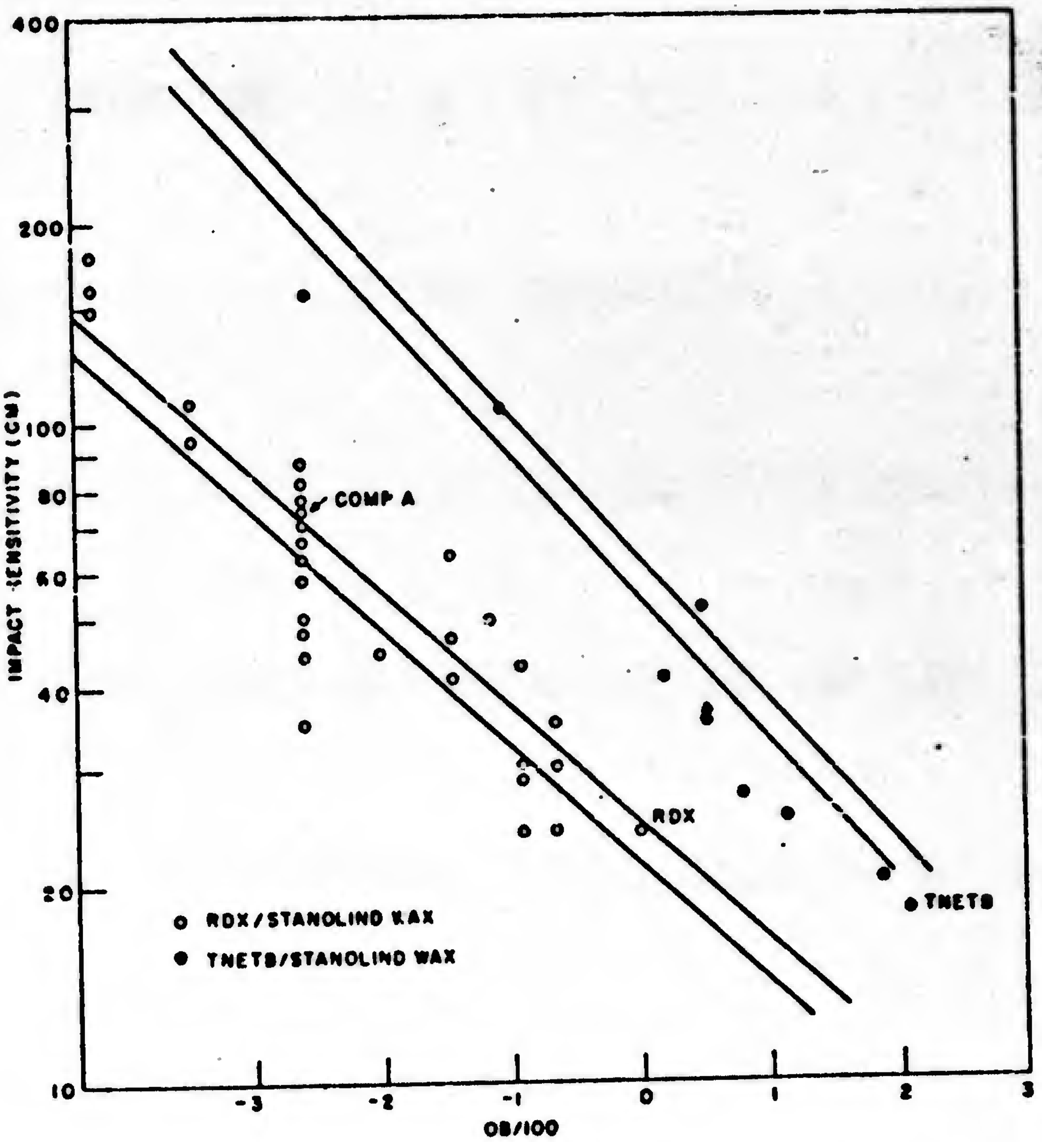

FIG. 5 "DESENSITIZATION" OF RDX AND TNETB WITH STANOLIND WAX

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