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FINAL REPORT

STUDY OF SUSCEPTIBILITY OF SOLID COMPOSITE PROPELLANTS TO EXPLOSION OR DETONATION

PHASE 2. FEASIBILITY STUDY OF DESENSITIZING ROCKET PROPELLANTS BY SUITABLE ATMOSPHERES

By

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Contract NOrd 18487 (FBM) Task 4

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1. INTRODUCTION

The control or, at least, the understanding of the sensitivity of explosives and propellants is in most applications desirable and in many applications imperative. Such applications range from hazards in manufacture, handling, and storage to accurate timing of deliberate initiation. Such control has been effected in the past by a careful choice of explosive, addition of phlegmatizers, and similar methods. Not infrequently, however, an explosive or propellant may behave erratically and show a much higher or a much lower sensitivity than usually, with corresponding effects in the application. Such irregularities cannot always be explained, and it appears that the sensitivity may depend upon factors other than those customarily considered decisive.

In the ideal case, the sensitivity should be controllable by means that do not affect deliberate initiation, nor the desired properties of the explosive or propellant. Such means should apply to the environment of the explosive or propellant, e.g., to the surrounding and included gas, or to the surface state of the solid or liquid material.

The work covered by this report is an experimental study of the feasibility of control of sensitivity by such external means. As such, it does not aim at elucidating the mechanism of initiation, nor does it aim at a practicable method of sensitivity control. It rather aims at obtaining evidence indicating whether such control is possible at all and in principle.

This work was preceded by a study of the literature. Pertinent published evidence is summarized and discussed in the appended Special Report No. 1310-62(01)SP, April 1961: The Mechanism for the Initiation of Detonation in Solid Explosives (Appendix A). This evidence indicates that control of sensitivity by such external means is feasible and also indicates a mechanism for the initiation. The mechanism indicated has been used as a working hypothesis in the experimental work. The experimental work has been designed to supplement published information.

Further references to the literature are given in the appended Special Report No. 1310-62(02)SP, March 1962: Initiation of Explosives by Friction (Appendix B) that also describes some pertinent exploratory experiments on the sensitivity of explosives to friction.

Conceivable external means for sensitivity control are choice of atmosphere and surface treatment. Assuming that initiation is effected by a chemical reaction on the surface of the material, addition of a catalyst or an inhibitor for this reaction, either to the surface or to the atmosphere in contact with the surface, would offer a means of control of this reaction and thereby of the sensitivity of the material. This thought forms the basis of the experimental work reported. The sensitivities of hydrazine perchlorate and RDX have been studied with samples in a few readily available gases and in contact with readily available metals.

The sensitivity of an explosive or a propellant is well defined in the nomenclature of the practice. Sensitivity means the sensitivity to initiation by impact or shock as determined by the dropweight test or the cardgap test. In addition, the usage offers qualified sensitivities, such as sensitivity to friction, sensitivity to bullet impact, thermal sensitivity, spark sensitivity, relating sensitivity to some other test or condition. To the purpose at hand, this meaning of sensitivity is adequate and the corresponding tests are equally adequate. The dropweight test has been used exclusively in this work. It will be described and discussed at length in Section 2.

A variety of objections may be raised against the dropweight test and the information that it supplies. These are of no major concern to the purpose at hand, but they are worth a reference in order to properly relate the data obtained to the practical requirements.

First of all, it should be stated in summary of the discussion in Section 2 that, in the course of these experiments, the dropweight test has been found to be remarkably accurate and reproducible. The spread of the data common in industrial testing may derive from lack of control of variables, e.g., moisture content, previous history of sample. Accuracy and reproducibility of the test as employed in this work are better than required by the purpose.

The main objection to the dropweight test is that sensitivity data obtained with 25 mg of a loose powder do not necessarily apply to a pressed or cast body of pound or ton size. This objection applies much less to a feasibility study than to the development of a practical method of sensitivity control. Clearly, it may be feasible to control the sensitivity of a small sample and not feasible to control the sensitivity of a large body, but this is an issue that must be left outside the scope of this investigation. It may be safely stated that if it is not feasible to control the sensitivity of a small sample, it is hardly feasible to control that of a large body, and before tackling the feasibility in the case of a large body one would do well starting out with a small sample.

Another major objection to the dropweight test is that it might not simulate the conditions encountered in practice, which might not be those of impact or of impact alone. The argument just presented also applies to this objection. Furthermore, the various modes of initiation of an explosive do not differ in their essential features as much as may appear. This point is discussed in the two appendices just referred to.

The effect of the atmosphere upon the sensitivity of explosives to impact has been reported fairly extensively in the literature. Such information has been supplemented by data obtained in this work. In the course of the work, it turned out that powder samples are unsuitable for the purpose because it is very difficult to replace the air entrapped in interstices between the grains. This phase of the investigation was then dropped and taken up again later with samples in the form of single crystals. The sensitivity of single crystals of RDX was then studied in different gases.

The dependence of the sensitivity upon the nature of the metal, with which the explosive is in contact, is much less treated in the literature. Some observations on the role of the metal in sensitivity to friction are referred to in Appendix B. Reference may also be given to the work of Bowers, Romans, and Zisman1) and of Soper2) on the effect of steel and copper inserts upon the sensitivity in the dropweight test and of Cook et al3) on the effect of various metals upon the sensitivity in the cardgap test. No further reports on this subject have been found in the unclassified literature.

In view of this scarcity of data, the effect of metals was particularly extensively studied in this work. This study included the effects of heat-treatment, coldwork, and thickness.

2. THE DROPWEIGHT TEST

As pointed out in Section 1, the sensitivity of an explosive is defined, according to common usage, in terms of the response in the dropweight test. This test has been used, and abused, extensively in routine technological testing of explosives, and, like most routine technological tests, has come to be regarded with suspicion by many scientific investigators. The reason is that this test shows spread and lack of reproducibility way beyond what is deemed permissible in research. It is our experience, however, that this is no inherent feature of the test, and that accuracy and reproducibility can be brought to a perfectly satisfactory level, better than 1% under favorable conditions, by controlling the pertinent variables. Since this point may be decisive to the significance of our data in the eyes of some readers of this report, it will be discussed at length in this section. The common sources of error encountered and the steps taken to eliminate them will be treated in relation to our particular test machine and more generally.

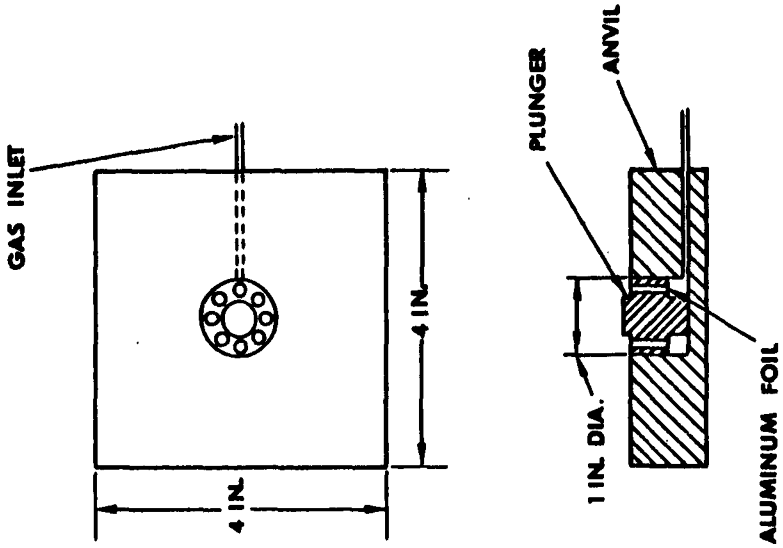
2.1 THE DROPWEIGHT MACHINE

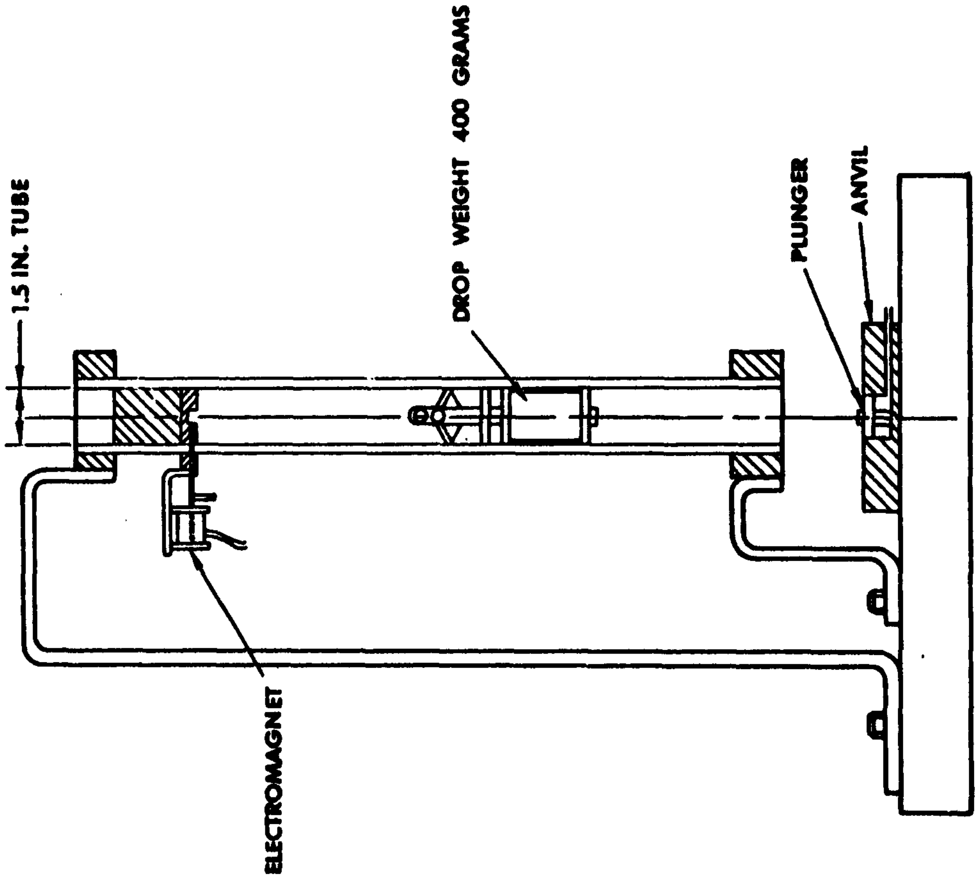
Standard dropweight machines (Picatinny Arsenal, Bureau of Mines) do not readily permit the control of the atmosphere around the sample. A special machine was therefore built to fit both phases of the work: different gases and different metals in contact with the sample.

Figure 1 shows the anvil and the plunger assembly. The anvil consists of a steel block in which a hole with a flat bottom is drilled, 1 in. in diameter and 15/16 in. deep. The plunger is of the same material, plow steel of 0.41% carbon. It has a surface of 1/2 in. diameter in contact with the sample and a surface of 1/2 in. diameter to be struck by the dropweight. These two surfaces are ends of cylinders protruding from a cylindrical body that fits snugly in the hole in the anvil. In this body, 12 holes of 1/8 in. diameter are drilled. The purpose of these holes is to offer an escape to the gaseous products of the sample. The holes are covered by a washer of aluminum foil that seals the chamber between anvil and plunger when the plunger moves downward. The gas pressure after initiation punches holes in the aluminum foil that offers little resistance to the escape of the gases. The holes punched serve as indicators of initiation and partial initiation.

The chamber between anvil and plunger can be evacuated and filled with any desired gas by means of two 1/4-in. holes drilled through the block and terminated by short pieces of tubing for connection to a vacuum pump and a gas supply. This anvil and plunger assembly was used in all the tests.

Exploratory tests were first conducted at the Downey facility. This required the dropweight machine to be small enough to go into an ordinary laboratory fume hood. The maximum height of fall was 51 cm. The dropweight was 400 g. Figure 1 shows the construction of this machine.


GAS INLET
4 IN.
4 IN.
PLUNGER
ANVIL
1 IN. DIA.
ALUMINUM FOIL


1.5 IN. TUBE
DROP WEIGHT 400 GRAMS
PLUNGER
ANVIL
ELECTROMAGNET

The dropweight is a cylindrical piece of steel shown in Figure 1. It is guided by a slotted tube as shown in Figure 1. This tube has holes drilled with a spacing of 1/2 in. through which a pin is inserted to hold the dropweight. This pin is retracted by an electromagnet to release the dropweight. The dropweight is fitted with a spring arrangement, as indicated in Figure 1, that prevents repeated striking after rebounce. Two springs are held by a ring that releases the springs as a result of the impact. The springs spring out and slide against the guide tube when the dropweight moves upward, and jam against the tube when the dropweight moves downward.

The use of this machine requires that the explosive is sensitive enough. Hydrazine perchlorate was used in all the tests with this machine.

In a later part of the program, the same anvil and plunger assembly was used in the Picatinny Arsenal type dropweight machine at the Chino facility. This machine is mounted on a block of concrete. The maximum height of fall is 70 in. Figure 2 shows a photograph of this machine. The dropweight weighs 2 kg. It strikes a cylinder of 1 in. diameter and 10-1/2 in. long that rests on the anvil.

Hydrazine perchlorate and RDX were tested in this machine.

In the experiments with different metals, thin wafers about 0.01 in. thick were inserted so as to cover the surfaces of anvil and plunger. In the experiments at Downey, these wafers were cut with shears and had a somewhat irregular form. In the experiments at Chino, punched circular discs of 15/16 in. diameter were used. These gave a better coverage of the steel surfaces. Comparative tests with copper and brass showed that the punched inserts gave a lower sensitivity than did the cut inserts.

2.2 TESTING PROCEDURE

The testing procedure was essentially the same for hydrazine perchlorate and RDX.

A lot of approximately 1 g was dried in a vacuum for at least 1 hr and then stored overnight in a desiccator. Samples of 25 mg were drawn from this lot, one at a time, as they were tested. It was found that both explosives were sensitive to moisture. The explosive was in powder form except in the tests with different gases, when small single crystals of 20 to 30 mg were used.

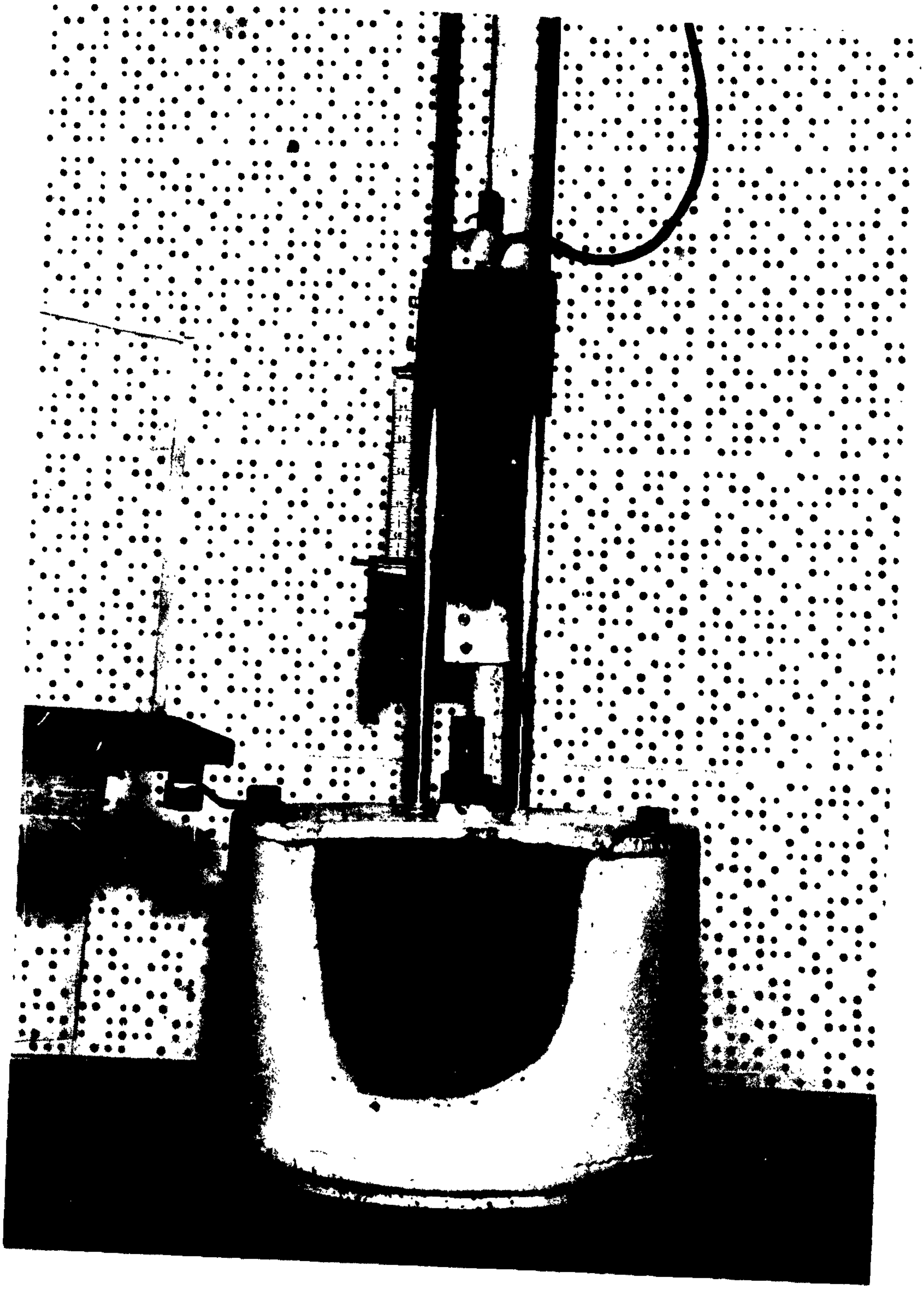


Figure 2. Dropweight Machine. Dropweight 2kg. Maximum Height 72 in.

The powder sample was taken from the lot by means of a little scoop so that the volume was always the same. The scoop was emptied into the hole in the anvil block so that the powder formed a neat cone in the center. When the sample was spread in a thin layer, no or partial initiation and rarely complete initiation occurred. When the sample was spread at random, the results were erratic.

The seal by the aluminum foil over the holes in the plunger turned out to be very important. With the holes open, i.e., without aluminum foil, the sample was very insensitive. A peculiar effect was observed at great heights of fall. With one aluminum foil only, the foil broke at the holes before initiation of the sample at, say, 70 in. of fall. There was then no initiation at this height. But the aluminum foil withstood the impact from, say, 20 in., and a sample was then initiated at this level. When double foils were inserted, the sample was initiated at all levels above 20 in. This effect cannot be explained by compression alone since the ports for introduction of gas were open. It appears that the production of a shock in the air would be more important.

It was observed that without the foil or when the foil broke, the powder sample was strewn over the anvil surface. Its sensitivity was reduced accordingly. This observation may be explained by local compression of the air within the pile of powder and a resulting wind outward that blew the powder pile apart. It may be pointed out in this connection that with the use of the aluminum foil the seal was good and independently of the fit of the plunger in the hole in the anvil. Consequently, there was no noticeable effect of wear of plunger and anvil upon the test data. Incidentally, the roughness or flatness of the surfaces in contact with the sample apparently did not affect the test data.

The seal by the aluminum foil did not permit evacuation of the chamber. In experiments at reduced pressure, the top of the plunger and the anvil around it were covered with a thin sheet of plastic that was pressed by the air pressure against the steel surfaces. In order to improve this seal, the steel surfaces were coated with a vacuum grease. This seal was also used in tests with different gases. In these tests single crystals of RDX were used. The air in the interstices between powder grains could not be removed effectively enough for the effect of the gas to show up. For a test in, e.g., N_2, the chamber was repeatedly evacuated and flushed with N_2. This procedure could not have removed all air from the chamber, but it was effective enough to show the differences between air and the other gases tested.

The initiation in several successive tests led to a marked rise of the temperature of the steel surfaces. This effect was not disturbing when metal inserts were used, but it was quite noticeable when bare steel surfaces were used. Before this effect was discovered, a test could show, say, five initiations at successively lower levels; the surfaces were then cleaned with acetone, which cooled them, and the next five samples then failed to initiate at successively increasing levels. In order to eliminate this effect, the sensitivity level was approached from below so that there was no heating by previous initiations. Furthermore, the chamber was cleaned with dry tissue in order to avoid cooling by a liquid cleaner, and finally, sufficient time, about 3 min, was allowed between successive tests to permit the surfaces to regain room temperature.

The most important variable in our experiments turned out to be the moisture content of the sample. This applies to RDX as well as to hydrazine perchlorate, although RDX is less sensitive to moisture than is hydrazine perchlorate. In all tests with different metal inserts or with different gases, the sensitivity of the sample was therefore checked in air and with bare steel surfaces before and after the test. Unless the level of the dry explosive under the standard conditions was reproduced, the lot was dried further until this reference level was established. It is our experience that storage in a desiccator does not ensure against pickup of moisture by the explosive. In the late fall, when the relative humidity at night is very high, the sensitivity tended to decrease unless special efforts were made to keep the moisture content down, e.g., by drying in a vacuum oven and storage in a vacuum desiccator. Of course, such measures do not ensure against moisture on the parts of the drop-weight machine. Moisture may also be picked up when the sample is transferred from the desiccator to the machine.

With a strict adherence to the procedure and the precautions described, the reproducibility of the data under normal conditions was very good and certainly good enough for the purpose of this investigation. The spread of the data within one determination and between repeated determinations was no more than 1/2 in. at a level above 20 in. With the hydrazine perchlorate the spread at the reference level, which was 1 in., was no more than 1/8 in. Under these conditions, an adequately defined level for initiation can be given, and there is no need for a 50% level as customarily reported.

It is worth mentioning that this degree of reproducibility is by no means uncommon but seems to have been experienced occasionally in most laboratories, even where thegeneral experience is one of very poor reproducibility. The good reproducibility seems to be common with samples out of one batch tested within a short period of time. The poor reproducibility seems to be common with samples out of different batches and with samples tested at different occasions. It also appears that the reproducibility is good with some types of explosives and poor with other types of explosives, presumably because different explosives are affected differently by impurities, moisture, decomposition in storage, and other factors, all of which may be difficult to control or to keep track of under operating conditions.

In the period December - January, the whether conditions were extreme with alternatingly very high humidities (fog, rain) and very low humidities (desert wind). It was then not possible, even with the precautions mentioned, to maintain a constant level of sensitivity of the explosive, and the work had to be interrupted for several weeks. In order for the work to continue, it was then necessary to permit some variation in the reference level of the sensitivity, i.e., the level of initiation with ambient air and bare steel surfaces. This reference level is given with the results.

It took somewhere between 10 and 20 tests to determine one level of sensitivity. The standard procedure was to have 10 tests within ± 1/2 in. at the level after the level had been located in a number of tests below and above the level.

It may be mentioned that the indication of initiation given by the holes punched in the aluminum foil by the gaseous products appears to be much more reliable than indication by sound or flame. In complete initiation, all the holes were punched. In partial initiation, one or a few holes were punched. In addition, unchanged parts of the sample were, as a rule, found after partial initiation. The case of partial initiation was rare. Such a result was disregarded, and the test was repeated at the same level.

3. EXPERIMENTAL RESULTS

The experimental results are given in Tables 1 through 7.

The accuracy of the sensitivity determination as estimated from reproducibility under normal weather conditions is ±1/8 in. below 5 in., ±1/4 in. between 5 and 10 in., and ±1/2 in. above 10 in. During the period of extreme weather conditions the reference level varies more than these accuracy figures. In order to allow for this error, the levels are given in whole inches and for the lowest levels with hydrazine perchlorate, to 1/2 in. These figures are considered significant.

Correction has been made in the tables (column marked "corrected") for the variation in reference level. All data for RDX powder have been reduced to a reference level of 19 in. by simply deducting the difference between actual reference level and 19 in. from the test level determined. The column marked "Test" gives the level as determined, without correction.

Another correction has been made for the mechanical effect of the metal inserts as explained in Section 4.2. The corrected levels thus indicate the chemical effect of the insert metal.

The data in Tables 1 through 5 comprise the effects of single inserts as well as that of pairs of inserts. When one insert was used, it was inserted between anvil and sample (bottom) or between plunger and sample (top).

4. DISCUSSION

4.1 EXPERIMENTAL DATA

Several investigators, e.g.$^{4-6)}$, have suggested that the spread of the dropweight test data is an inherent feature of the initiation and attempted to treat data on the basis of a random distribution of spots of different sensitivities or of different received energies. This view appears to be based upon experimental data obtained under poor control of the variables. Thus, Taylor and Weal$^{4)}$ obtained initiation at all levels between 2.0 cm and 3.5 cm in one instance. In such a case, all the samples may have been initiated at the lowest level or at a still lower level, had the variables been properly controlled.

Table 1a. Test Results with Hydrazine Perchlorate with Two Identical Metal Inserts and Ambient Air — 400 g Dropweight.

Metal Inserted	Thickness (in.)	Treatment	Height (cm)
None			25
Aluminum (99.5%)	0.001	as received	> 51
Aluminum (99.99%)	0.005	as received	> 51
Brass	0.003	as received	> 51
Brass	0.010	as received	> 51
Copper	0.010	as received	> 51
Stainless 304	0.005	as received	51
Stainless 410	0.004	as received	41
Stainless 410	0.025	as received	> 51
Stainless 410	0.025	short anneal	> 51
Stainless 410	0.025	long anneal	> 51
Steel 1095	0.005	as received	41
Steel 1095		quenched from 920°C, aged at room temperature 10 hr	28
Steel 1095		quenched from 920°C, aged at room temperature 15 min	36
Steel 1095		quenched from 920°C, tempered at 300°C, aged at room temperature 10 hr	21
Steel 1095		quenched from 920°C, tempered at 300°C, aged at room temperature 15 min	23

Table 1b. Test Results with Hydrazine Perchlorate with Two Identical Metal Inserts and Ambient Air — 2 kg Dropweight.

Metal Insert (thickness, in.)	Height, in.			Remarks
	Test	Reference	Corrected	
None	1.0	1.0	1.0	
0.007 spring steel	6.5	1.0	2.5	
0.004 410 steel	6.5	2.0	-1.5	
0.017 410 steel	12.5	1.5	-1.0	
0.004 304 steel	18	1.5	13.5	
0.004 304 steel	35	1.5	30.5	Pickled in 7.5N HNO_2 for 2 hr
0.001 Al	6.25	1.0	5.25	
0.005 Cu, soft	13	1.0	12	
0.010 Cu, soft	70	1.5	64	
0.010 Cu, soft	> 72	1.5	> 53	
0.010 Cu, hard	> 72	1.5	> 69	
0.010 Cu, hard	68	1.5	65	Annealed at 630°C for 1 hr
0.005 brass	20	1.0	14	
0.010 brass	48	1.5	38	
0.010 brass	46	1.5	35	Pickled in NH_4OH for 24 hr
0.010 brass	42	1.5	32	Pickled in NH_4OH for 48 hr

Table 2. Test results with inserts of different metals in ambient air. Height 51 cm. One test with each combination. X = detonation, O = no detonation.

		No Insert	Aluminum 99.5%	Aluminum 99.99%	Brass 0.003 in.	Brass 0.010 in.	Copper	Stainless 304	Stainless 410, .004 in.	Stainless 410, .025 in.
No Insert	**Top**	X	X	X	X	O	X	X	X	X
	Bottom	X	X	X	X	O	O	X	X	X
Aluminum, 99.5%	**Top**	X	O	O	O	O	O	X	O	O
	Bottom	X	O	O	O	O	O	O	X	O
Aluminum, 99.99%	**Top**	X	O	O	O	O	O	O	X	O
	Bottom	X	O	O	O	O	O	O	O	O
Brass, 0.003 in.	**Top**	X	O	O	O	O	O	O	O	O
	Bottom	X	O	O	O	O	O	O	O	O
Brass, 0.010 in.	**Top**	O	O	O	O	O	O	O	O	O
	Bottom	O	O	O	O	O	O	O	O	O
Copper	**Top**	O	O	O	O	O	O	O	O	O
	Bottom	X	O	O	O	O	O	O	O	O
Stainless 304	**Top**	X	O	O	O	O	O	X	O	O
	Bottom	X	X	O	O	O	O	X	O	O
Stainless 410, 0.004 in.	**Top**	X	X	O	O	O	O	O	X	O
	Bottom	X	O	X	O	O	O	O	X	O
Stainless 410, 0.025 in.	**Top**	X	O	O	O	O	O	O	O	O
	Bottom	X	O	O	O	O	O	O	O	O

Table 3a. Test Results with Hydrazine Perchlorate with Two Different Metal Inserts and Ambient Air — 400 g Dropweight.

Metal Insert (thickness, in.)		Height, cm	Remarks
Top	Bottom		
Cu	None	> 51	
None	Cu	49	
0.001 Al	0.005 304 steel	49	99.5% Al
0.005 304 steel	0.001 Al	> 51	99.5% Al
0.001 Al	0.004 410 steel	> 51	99.5% Al
0.004 410 steel	0.001 Al	49	99.5% Al
0.005 Al	0.004 410 steel	49	99.99% Al
0.004 410 steel	0.005 Al	> 51	99.99% Al

Table 3b. Test Results with Hydrazine Perchlorate with Two Different Metal Inserts and Ambient Air — 2 kg Dropweight.

Metal Insert (thickness, in.)		Height, in.		
Top	Bottom	Test	Reference	Corrected
0.001 Al	0.001 Al	6.5	1.0	5.5
None	0.001 Al	3.5	1.0	3.5
0.001 Al	None	2.5	1.0	2.5
0.005 Cu, soft	0.005 Cu, soft	13	1.0	12
None	0.005 Cu, soft	7	1.0	6
0.005 Cu, soft	None	4	1.0	3
0.005 brass	0.005 brass	18	1.0	8
None	0.005 brass	3.75	1.0	2.25
0.005 brass	None	3.75	1.0	2.25

Table 4. Test Results with RDX with Two Identical Metal Inserts and Ambient Air — 2 kg Dropweight. Corrected Values by Deduction of Mechanical Effect of Inserts as Shown in Table 6.

Metal Insert (thickness, in.)	Height, In.			Remarks
	Test	Reference	Corrected	
0.007 1095 steel	46	18	43	
0.007 1095 steel	41	18	38	Annealed at 1000°C for 1 hr
0.004 410 steel	36	18	30	
0.004 304 steel	56	19	52	
0.004 304 steel	67	19	63	Pickled in 7.5N HNO_2 for 2 hr
0.001 Al	17	17	19	
0.004 Al	40	19	28	
0.005 Cu, soft	53	18	53	
0.010 Cu, soft	> 72	19	> 66	
0.016 Cu, soft	> 72	18	> 54	
0.010 Cu, hard	> 72	18	> 70	
0.010 Cu, hard	> 72	18	> 70	Annealed at 630°C for 1 hr
0.005 brass	47	17	43	
0.010 brass	> 72	18	> 61	

Table 5. Test Results with RDX with Two Different Metal Inserts and Ambient Air — 2 kg Dropweight.

Metal Insert (thickness, in.)		Height, in.		
Top	Bottom	Test	Reference	Corrected
0.007 1095 steel	None	23	18	24
None	0.007 1095 steel	24	18	25
0.001 Al	None	15	19	15
None	0.001 Al	15	19	15
0.004 Al	None	15	17	13
None	0.004 Al	17	17	15
0.005 Cu, soft	None	38	17	39
None	0.005 Cu, soft	35	17	36
0.010 Cu, soft	None	> 72	17	> 68
None	0.010 Cu, soft	40.5	17	36
0.005 brass	None	36	17	32
None	0.005 brass	40	17	36
0.005 Cu, soft	0.007 1095 steel	36	17	37
0.007 1095 steel	0.005 Cu, soft	36	17	37
0.004 410 steel	None	29	18	20

Table 6. Test Results with RDX in Ambient Air and Metal Inserts Between Plunger and Dropweight.

Metal Insert (thickness, in.)	No. of Inserts	Height, in.		
		Test	Reference	Mechanical Effect
0.005 mild insert	2	22	19	3
0.007 1095 steel	1	15	15	0
	2	19	15	4
0.004 410 steel	1	21	19	2
	2	26	19	7
	3	31	19	12
	4	36	19	17
0.017 410 steel	1	31	19	12
0.004 304 steel	1	18	15	3
	2	19	15	4
0.001 Al	1	15	15	0
	2	16	15	1
0.004 Al	1	19	15	4
	2	31	19	12
0.010 Al	1	45	21	24
	2	> 72	21	> 51
0.005 Cu, soft	1	22	21	1
	2	22	21	1
	3	23	21	2
0.010 Cu, soft	1	18	15	3
	2	21	15	6
0.016 Cu, soft	1	25	16	9
	2	35	16	19
0.010 Cu, hard	1	21	21	0
	2	24	21	3
0.010 brass	1	27	21	6
	2	31	21	10

Table 7. Test Results with Single Crystals of RDX in Different Gases. Corrected Values by Deduction of Mechanical Effect of Inserts as Shown in Table 6.

Metal Insert (thickness, in.)		Gas	Height, in.		
Top	Bottom		Test	Reference	Corrected
None	None	Air	33	33	33
		Vacuum	39	39	33
		O_2	30	33	30
		N_2	64	39	58
		A	> 72	33	> 72
		He	45*	33	45*
		Dried He	> 72	33	> 72
None	0.005 Cu, soft	Air	63	33	63
		O_2	61	35	59
		N_2	> 72	33	> 72
		He	60	35	58
None	0.004 304 steel	Air	64	35	59
		O_2	62	35	57
		N_2	> 72	35	> 67
		He	72	35	67

* Partial initiation from 45 in. up to 72 in.

To the purpose of this investigation the spread of the data is of little significance as long as it is negligible at the side of the differences observed with different insert metals and with different gases. Indeed, to the main purpose of this investigation, an error of a few, even of 10 in. would be negligible at the side of the effect of copper inserts upon the sensitivity of hydrazine perchlorate or of argon upon the sensitivity of RDX crystals. Nevertheless, in order to make full use of the data obtained, all differences in sensitivity greater than the experimental error will be considered significant.

The experimental error in the sensitivity data with different inserts is composed of two parts. One part derives from inadequate control of the experimental variables. This error is estimated to be less than 1 in., assuming an error of 1/2 in. in the test and in the reference. The second part depends upon the use one wants to make of the data. In some applications it may make no difference whether the effect of an insert metal is a mechanical effect or a chemical effect. But in order to discuss the chemical effect it is necessary to deduct the mechanical effect. As discussed in Section 4.2, the data given in Table 6 give upper limits for the mechanical effect. The "corrected" levels given in the tables have been obtained by deducting from the observed level the difference in level obtained with the explosive between bare steel surfaces when two wafers were inserted between rod and plunger as shown in Table 6.

4.2 MECHANICAL EFFECTS OF METAL INSERTS

It has been suggested that different metals in contact with an explosive affect the sensitivity to impact according to their heat conductivities.1) This view is refuted by our data. Aluminum and copper are outstandingly good heat conductors, and type 304 stainless steel is an outstandingly poor heat conductor, but there is no relation between the sensitivity of the explosive and the heat conductivities of these metals.

It has been suggested that the effect of metal inserts upon the sensitivity is related to the hardness of the metal inserted, the sensitivity increasing with the hardness of the metal.2) This view is also refuted by our data. The effect of heattreatment rather indicates that the sensitivity decreases with increasing hardness for a given metal.

It has been suggested that an insert reduces the sensitivity by a cushioning effect of the insert.2) This effect is almost obviously present. Experiments were conducted to investigate the magnitude of this effect.

The acoustical properties, sound velocity v, density ρ, and acoustical impedance $z = v\rho$, for the metals used are given in Table 8.

Table 8. Acoustical Properties of Metals.

Metal	Sound Velocity v m/s	Density ρ g/cm	Acoustical Impedance $z = v\rho$
Aluminum	5,100	2.7	13,800
Brass	3,500	8.5	29,800
Copper	3,560	8.9	31,700
Steel	5,000	7.7	38,500

The corresponding properties for the explosive are not known but may be roughly estimated to $v = 1400$ m/s, $\rho = 1.4$ g/cm, $z = v\rho = 2000$.

The effect of heattreatment and coldwork on the numbers given for the metals are not known but are probably small as compared to the differences between the different metals.

The transmission of pressure through the interface between two media 1 and 2 is

$$\frac{2 z_1}{z_1 + z_2}$$

If subscripts 1 and 2 denote steel and insert metal and subscript 3 denotes the explosive, the transmission to the explosive is that given in Table 9a.

Table 9. Transmission of Impact Pressure to Explosive.

	a. Transmission only	b. Transmission and reflection
No insert	0.10	0.090
Aluminum insert	0.13	0.098
Copper insert	0.11	0.097

The reflection at the bottom side of the explosive is

$$\frac{z_2 - z_3}{z_2 + z_3}$$

The fraction of the impact pressure that is transmitted to the explosive and then reflected back into the explosive is given in Table 9b.

It may be concluded from this type of crude calculation that the acoustical impedance of the insert metal does not correlate with the observed effect of the metal upon the sensitivity of the explosive.

With a thin wafer as used in our experiments the cushioning effect would not be expected to be determined by the metal as such but rather by the deformation of the warped wafer. This effect was studied by putting inserts between the steel surfaces of the rod and the plunger. As would be expected, the harder and thicker inserts gave the greater reduction in sensitivity. The data are given in Table 6.

In the transfer of impact from one steel surface to another, the intermediate insert is first flattened, with a corresponding loss of energy. The amount of energy lost increases with the amount of deformation of the insert. This is clearly shown by the larger loss of energy with a stack of thin inserts as compared to that with a single thick insert. In the transfer of impact from a steel surface to the soft sample, however, the intermediate insert need not be flattened, and the loss of energy by this effect should therefore be smaller.

Clearly, the softer the metal insert, the less energy is spent in its deformation. This is shown by the data for steel and copper in Table 6. Yet, the soft copper gives a lower sensitivity than the hard steel.

Finally, it should be pointed out, the warping could not possibly be the same for all the inserts of a given material. Hence, the energy loss in flattening the insert, if significant, should show up as a spread of the sensitivity test data. This spread is negligible at the side of the total effect upon the sensitivity observed.

The data given in Table 6 support the view that the acoustical impedance of the insert, and thereby reflection of shock against the insert, has no noticeable effect upon the shock transmission to the explosive and that this effect is negligible at the side of the loss of energy in the deformation of the insert.

To the main purpose of this investigation, it makes little difference whether the effect of the insert is mechanical or chemical in nature. However, it makes considerable difference to the course to be taken in the development of sensitivity control methods. It is therefore desirable to separate the two effects. The data reported in Table 6 make this separation possible to a certain degree of approximation. The "corrected" levels in the tables are the observed ("test") levels less the variation in reference level. As already pointed out, the correction for the mechanical effect is too large. As a consequence, the corrected levels are lower limits. In some cases the corrected levels are even negative.

4.3 CHEMICAL EFFECTS OF METAL INSERTS

The experimental results are compatible with a catalytic effect of NO and OH radicals upon the rearrangement in the solid state and thereby upon the initiation. For further evidence to the chemistry of the initiation, reference is made to Appendices A and B.

The chemical effects of the metals upon these species have been studied in connection with the kinetics of their dissolution in aqueous nitric acid solutions.

Iron and annealed carbon steel do not reduce the NO_2 radical in undissociated $HONO_2$. When hydrogen is present in the metal, however, such reduction occurs and promotes the dissolution in concentrated nitric acid. Thus, whereas Armco iron and annealed carbon steels are passivated by nitric acid above 7.2N, quenched spring steel is not passivated even in 15N nitric acid. The reason is that the quenched steel contains a hydrogen-rich phase, ϵ-carbide.7) This carbide is transformed and its hydrogen removed by tempering at 300°C. An investigation of the effects of heat-treatment and carbon content upon hydrogen content and passivated in nitric acid is reported in Appendix C. The effect of the hydrogen-rich ϵ-carbide is particularly conspicuous in the behavior of quenched type 410 stainless steel, in which ϵ-carbide is stabilized by the chromium. Whereas the annealed steel is passivated by nitric acid of very low concentrations, below 1N, the quenched steel dissolves rapidly in 15N nitric acid.

Iron and steel react with the NO radical to form iron nitrosyl compounds. Under the conditions at hand, this reaction is probably slow as compared to the reduction of the NO_2 radical by hydrogen. Coldworked steel contains nitrogen in a surface layer, and this nitrogen probably reacts more rapidly with the NO radical to form N_2 than does the iron to form nitrosyl.

Iron and steel decompose H_2O into H and OH. They thus promote the formation of OH.

Copper does not dissolve in dilute nitric acid but dissolves rapidly in concentrated nitric acid. The rate is proportional to the concentration of undisociated nitric acid.[8,9)] Copper reduces the NO_2 radical. It does not react at an appreciable rate with the NO radical. Copper does not decompose H_2O and therefore does not promote the formation of OH. On the contrary, copper destroys OH by decomposing pairs of OH radicals or H_2O_2 molecules into oxygen and water.

Brass has the same effects as the copper that it contains. But the zinc in the brass favors the formation of OH by decomposing H_2O.

Aluminum reacts very slowly with aqueous nitric acid. The rate of dissolution is comparable to that of passive iron. The dissolution occurs essentially by the formation of hydroxide by reaction with water and the subsequent reaction of the hydroxide with dissociated nitric acid to form soluble nitrate.[10)] Aluminum does not react with NO and NO_2 radicals. Aluminum is a powerful catalyst for the formation of hydrogen peroxide. Pure aluminum does not decompose H_2O_2 into 2 OH, but iron present in the aluminum or in its vicinity effects this decomposition.

These chemical effects of the insert metals are reflected by the sensitivity data.

The highest sensitivity is obtained with aluminum and iron together, i.e., with a single insert of aluminum and one bare steel surface. This is a result of formation of H_2O_2 on the aluminum and its decomposition into 2 OH on the steel. With two aluminum inserts the sensitivity is low because the H_2O_2 is not decomposed into OH.

The lowest sensitivity is obtained with copper because it destroys both NO_2 and OH radicals. Brass is slightly less effective in these respects, owing to the zinc present, and therefore gives a slightly higher sensitivity.

The effects of coldwork and heattreatment are particularly conspicuous with the spring steel. The lowest sensitivities are obtained with N-bearing coldworked steel and H-bearing quenched steel. The tempering of the quenched steel at 300°C transforms the ϵ -carbide and removes the hydrogen and thereby eliminates the desensitizing effect of the hydrogen.

The effect of nitrogen in steel is shown in the results with stainless steel inserts. Type 304 (austenitic) stainless steel contains much more nitrogen than does type 410 (ferritic) stainless steel. With inserts of the same thickness, 0.004 in., the sensitivity with 410 inserts is higher than that with 304 inserts. It was thought that the 304 material may have become partly ferritic on the surface as a result of coldrolling. Inserts of this material were therefore pickled in 7.5N nitric acid for 2 hr and the test was repeated. The sensitivity was then lower. This experiment, which was performed with both hydrazine perchlorate and RDX, seems to show conclusively that the surface material decides the sensitivity, and that austenite gives a lower sensitivity than does ferrite. It should be noted that in the particular case of type 304 stainless steel coldwork actually reduces the nitrogen content in a surface layer. But in the case of the spring steel, coldwork increases the surface nitrogen with a corresponding lowering of the sensitivity.

It was thought that pickling of brass in NH_4OH solution would cause nitrogen enrichment at the surface of the brass. Accordingly, brass inserts were pickled for 24 hr and for 48 hr and tested with hydrazine perchlorate. The effect of the pickling was to increase the sensitivity. It is possible that this result was caused by removal of a coldworked nitrogen-rich surface layer.

4.4 THE EFFECT OF THICKNESS OF METAL INSERTS

In almost all the cases of metal inserts of different thicknesses, the thicker insert gave the lower sensitivity. In the case of hydrazine perchlorate and type 410 stainless steel, the thickness effect is essentially a mechanical effect, and the insert is chemically little different from the steel in anvil and plunger. But in the case of RDX and 410, the mechanical effect does not suffice to account for the great reduction in sensitivity.

A peculiar thickness effect is shown by the aluminum inserts with RDX. In this case the sensitivity was the same or even somewhat higher with the thicker insert when one insert was used, although it was lower when two inserts were used. This result cannot be explained by penetration of the sample through the thin metal.

The information available is insufficient for conclusions and even for a discussion of the thickness effect. In order to indicate the type of information required and the lines along which a chemical effect of thickness may be sought, a few speculations will be offered.

The instances mentioned may suffice to show that the thickness may have a chemical effect in addition to the obvious mechanical effect. In the case of hydrogen-bearing steel, the effect of increased thickness may be to increase the volume of hydrogen available for surface reactions. The same may apply to nitrogen-bearing metals. This may be the explanation of the thickness effect with RDX and type 410 stainless steel and also with RDX and hydrazine perchlorate and brass.

A thickness effect that appears particularly difficult to explain is that of soft copper. However, the data for hydrazine perchlorate show that annealing of the hard copper produces a soft copper that gives a higher sensitivity than does the so-called soft copper of the same thickness. It is therefore not altogether inconceivable that even the soft copper may have enough of the coldwork effect for the nitrogen content to be decisive. In the case of copper, coldwork may also be expected to cause intercrystalline oxidation, but the effect of this phenomenon is hard to estimate.

4.5 COMPARISON WITH INITIATION BY SHOCK

An investigation of initiation by shock as in the airgap test is currently pursued under another contract. In this investigation, 8.3 g of RDX powder is compacted into a sealed metal cup and initiated by the shock from a pressed tetryl charge of 8.7 g weight. Table 10 shows the main results.

Table 10. Critical Air Gaps (mm) for RDX in Cups of Various Metals

Steel as drawn	46.4
Aluminum as drawn	50.5
Copper as drawn	39.5
Brass as drawn	41.8

It is gratifying to note that the sensitivity of the explosive is affected in the same manner by the metal in the airgap test as in the dropweight test. This supports the conclusion that the effect of the metal is essentially chemical in nature, and also the conclusion that the initiation process contains chemical reaction as an essential element.

4.6 EFFECTS OF SURROUNDING GAS

An effect of the surrounding gas upon the sensitivity of explosives has been reported by several investigators. References to such work are given in Appendix A. Generally speaking, the sensitivity as compared to that in air is lower in noble gases and higher in the gaseous decomposition products of the explosive. These observations were confirmed in our tests with single crystals of RDX. The data in Table 7 show a conspicuous difference in sensitivity between air and argon or helium.

Bottled gases are generally comparatively pure and, in particular, drier than ambient air. In view of the large effect of moisture upon the sensitivity, it is conceivable that the effect of the gas is essentially to dry the explosive and thereby to make it more sensitive. This aspect of the effect of the surrounding gas was carefully considered. It shows up clearly in the results with powder samples of hydrazine perchlorate shown in Table 11. In these experiments it was not possible to remove all the air from the interstices between the powder particles, and the affect of drying the air and the powder therefore was greater than that of replacing the air by the gas. As a result, the sensitivity in argon was higher than that in ambient air.

Table 11. Test Results for Hydrazine Perchlorate Powder with Bare Anvil and Plunger Surfaces and Various Gases.

Gas	Height, cm
Ambient air	25
Dried air	25
O_2	29
"Pure" N_2	29
Dried N_2	29
NO	22
Argon	17

With single crystals of RDX the air is comparatively easily removed. The effect of the gas is then conspicuously different as shown in Table 7. In this case, there was no initiation in argon or dried helium at 72 in., the highest level that the machine permitted. It is remarkable that the trace of air in the commercial argon did not suffice for initiation on bare steel surfaces.

Another remarkable result is that helium gave partial initiation at all levels above 45 in., but no complete initiation even at 72 in. In helium conducted over Dryerite there was no initiation, not even partial initiation, up to 72 in.

A few experiments were conducted with combinations of gas and metal insert. There was no initiation in A, He, or N_2 with two inserts, and one insert only was therefore used in these experiments. The results show that the effects of gas and insert are not additive.

It is hard to tell to what extent air was replaced by the purging gas in these experiments. The data show much less sensitivity in an inert gas than in air or O_2, but they do not show the full magnitude of the effect, either because the height of the machine was insufficient for initiation, or because the air was not perfectly removed.

5. CONCLUSION

The results with various metal inserts and with various gases show conclusively that the sensitivity to initiation in the dropweight machine can be drastically reduced by a suitable choice of metal or gas in contact with the explosive. It follows that the sensitivity of a given explosive or propellant can be controlled by such external means.

Although, thus, the feasibility of such sensitivity control has been demonstrated, its technical application raises problems that fall outside the scope of this investigation. These problems may be mentioned without any attempt at evaluation of their magnitudes. They would require study on the development level.

The experiments were conducted with small samples, the grains of which were all within a short distance from the metal inserts. It may be expected that the metal inserts would have a smaller effect on large bodies of explosive or propellant. The effect of the surrounding gas requires that the air be effectively removed from the sample. This may offer difficulties with large quantities of powder or pressed material.

An important result of this investigation is that initiation occurs by chemical reactions that may be controlled by external means. This result should be contrasted to the common belief that heat alone is decisive in initiation and that initiation occurs at hot spots. The control of chemical reactions is fairly simple, whereas no way can be seen how to control the formation of hot spots.

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APPENDIX A

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THE MECHANISM FOR THE INITIATION OF DETONATION IN SOLID EXPLOSIVES

by

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ABSTRACT

Evidence on the chemical effects of shock and the conditions for the initiation of detonation of solid explosives by shock, as well as rate data on the decomposition of solid explosives, are reviewed. It is concluded that the initiation is caused by certain species, primarily H and OH and secondarily by HNO and HONO, formed by the shock and by reactions during the induction period. The role of the latter species is to catalyze rearrangement in the solid, presumably by the formation of suitable structures.

1. INTRODUCTION

Our knowledge of initiation of explosives is reflected by our safety measures against accidental explosions in the manufacture, storage, and handling of explosives. The only measure in which anyone has confidence is to keep the quantities of explosives and the number of personnel present at a minimum in order to keep damage and loss of life at a minimum.

Yet, no hazard has attracted attention and effort on a scale comparable to that of explosives. Nature, extent, and implications of this hazard are such that safety must be secured at any cost. Clearly, much of the writing on the subject aims merely at quieting local personnel and population, but an enormous amount of serious study has been devoted to the subject both on scientific and engineering levels. One may then well ask why this effort has not yielded tangible results.

At this point it may be wise to point out that this paper does not pretend to solve the problem. Its purpose is to emphasize an approach that has not been pursued to the extent that it is promising. This approach has been formulated by Weyl and Marboe1) and probably by numerous investigators before them and later: "The physics of explosives require mechano-chemical explanations for improved understanding. Most modern explosives must be initiated by a shock wave and the reason for the lack of understanding of the phenomenon is due to a purely mechanical approach. The processes going on in front of a detonation wave are mechano-chemical in nature."

The explosion is certainly a chemical effect since it converts a solid explosive into gaseous decomposition products. The essence of the problem is then how mechanical cause is converted into chemical effect.

The current theory is primarily concerned with the conversion of mechanical into thermal energy. This is certainly an important aspect of the process. However, temperature as such does not initiate or cause chemical reaction, it merely affects the rate of chemical reaction. Another as important aspect of the process is the nature of the chemical reaction affected by the temperature. This latter aspect has received comparatively scant attention in the past. It is the subject of this discussion.

Shock is known to have chemical effects. Thus, it produces in air such reactive species as H, OH, and the oxides of nitrogen. Shock is also known to be enormously activated as initiator of explosion by the presence of air in small pockets. This is not due merely to an increased efficiency in the conversion of mechanical energy into heat, for different gases have different effects far beyond their thermo-mechanical differences. Furthermore, numerous instances are known of initiation as the shock leaves the solid, whereas the heat effect should be expected to be greatest where the shock strikes the solid. It appears then that shock primarily affects the air, and that the air by exposure to shock acquires ability to initiate explosion of the solid.

The products of shock in air are also known to be formed in slow thermal reaction prior to explosion. When $NH_4\ NO_3$ is heated, it decomposes into NH_3 and HNO_3. The NH_3 may then be converted into NO and the NO further, presumably, into HNO and HONO. Explosion occurs when this conversion of NO has proceeded for some time. When NH_3 is evolved without formation of NO, no explosion occurs. This is typical of initiation of explosives in general.

In addition to such experimental evidence as that just referred to, there are general principles for chemical change that must be satisfied by the mechanisms of initiation. The decomposition of a solid into gaseous products, e.g., of $NH_4\ NO_3$ into NH_3 and HNO_3, requires a rearrangement of atoms or radicals and of bonds, e.g., the transfer of an H atom from the NH_4 group to the NO_3 group. Such rearrangement is the essence of chemical synthesis and has been studied extensively in cases other than explosion. It is greatly affected by solid and gaseous catalysts. Particularly effective promoters of H rearrangement are NO (nitrosyl) and NO_2 (nitronium) groups. The effect of such catalysts and promotors is such as to suggest that their formation determines the rate of rearrangement when they are not deliberately added.

This discussion is concerned primarily with the initiation and only secondarily with the propagation. The initiation is invariably associated with some delay, an induction period, during which comparatively slow processes occur. These slow processes are accessible to observation and analysis. They may well be assumed to follow general rules for such slow processes. Accordingly, a wealth of pertinent evidence is available. This evidence is insufficient for the derivation of the mechanism of initiation, but it is sufficient for the design of experiments to elucidate the mechanism. Clearly, the initiation cannot be entirely divorced from the propagation since the slow processes during initiation ultimately create the conditions for propagation. On the other hand, this ultimate result occurs only if the initiating process proceeds in the required manner. From the point of view of sensitiveness we are therefore concerned with the initiation process alone. An effort toward reducing the hazard of explosives should be directed toward suppressing initiation rather than toward quenching of propagation.

2. EFFECTS OF SHOCK UPON GASES

Shock waves in gases are known to produce effects which are not produced by merely heating the gas. The conspicuous effects are ionization and luminosity. It has also been established by analysis that certain species, particularly NO[2-9)] and OH[10)], are formed at rates and concentrations above those to be expected from heating the gas to the same temperature. These effects will be discussed and correlated in the following.

The ionization of gases by shock waves occurs by some unknown mechanism that has attracted scant attention only. It has been observed that ionization by shock waves in argon is initiated by an unidentified impurity[11)]. The predominating ionized species in H_2-O_2 mixtures exposed to shock waves is NO, which is formed from the N_2 present as an impurity[9)]. These effects should be related to the role of impurities in the afterglow of gases that does not occur unless N_2 and O_2 are present; it is generally attributed to the oxidation of NO.

Flames in explosive gas mixtures may be suppressed or even quenched by means of fine powders[12-14)] and by wire gauzes[15)]. This effect cannot be explained by the cooling effect of the powder or wire gauze, because the effectiveness of a powder is not related to its thermal properties.

The current theory of chain reactions in gases postulates that reactions occur as a result of random collisions between the reacting species. This postulate is not satisfactory. It appears indeed that the collisions ought to be highly preferential in order to account for the rate of reaction in the chain and for the length of the chain. It also appears that ionization may cause such preference. Whether this view is stated or implied, it seems to be reflected by the increasing frequency of publications on ionization in flames.

Accordingly, deionization of a flame or a shock wave should quench the flame or the detonation. The effect of the powder just referred to seems to be precisely that.12)

It was reported by Fay16) that H_2-O_2 mixtures are ignited by a shock wave of a velocity 1.55 times that of sound or more. This velocity is close to the average velocity of the molecules. The calculated temperature behind the weakest initiating shock wave was 130°C, which is considerably below the adiabatic compression ignition temperature of 546°C.

Closely related to the chemical effects of shock are those of ultrasound. The effect of ultrasound on aerated water or moist air is essentially the formation of OH and its products: H_2O_2, O_3, NO, HNO_2, and HNO_3.

3. THE INITIATION OF DETONATION BY SHOCK

A shock wave of sufficient intensity initiates detonation of solid explosives. This process has been studied in considerable detail and the experimental evidence is to some extent conclusive.

A remarkable feature of this initiation is that the detonation does not start at the surface where the shock strikes but at some distance from the surface. This delay has been studied by several investigators.17-26) Dr. E. G. Whitbread has prepared a movie showing the effect very clearly.

Frequently the initiation occurs after the shock wave has left the solid. This effect is shown in pictures published by Eichelberger and Sultanoff.23, 26) Donor and receptor are separated along their length by a metal plate. The shock wave from the donor goes through the plate and through the receptor, and the initiation occurs at the back surface of the receptor as the shock emerges into the air. Whitbread27) has studied this phenomenon using single crystals of RDX. It makes little difference whether the wave is reflected back into the explosive as a compression or as a rarefaction. However, the sensitivity expressed in terms of the distance between donor and receptor depends strongly upon the nature of the reflector.

It was shown by Bowden24-26, 28) and has since been confirmed by numerous investigators that the initiation by shock is enormously facilitated by small air bubbles in the explosive or in the fallhammer. Bowden et al26, 29) were able to take pictures of such air bubbles during the impact. The first noticeable effect of the impact is a tiny spot of light in the air bubble. A flame spreads from this spot at a velocity of 20 m/s. After 50 µs it bursts through the cavity wall, and the explosive detonates.

Bowden et al 30) also tried different gases in such bubbles. Typical figures for the explosion efficiency at a gas pressure of 64 mm Hg and a constant fallhammer energy are: air 40/51 (78%), N_2 5/5 (100%), either 0/8 (0%), CCl_4 0/6 (0%). At 760 mm Hg, air and N_2 gave 90% efficiency, 36/40 and 14/16, respectively, whereas H_2 gave only 4/17 (24%).

Evans and Yuill 26, 29) studied the effect of compressed gases in the initiation of various explosives by using a cylinder in which the gas could be adiabatically compressed to a predetermined ratio. The temperatures at which ignition occurred were considerably higher than the conventional ignition temperatures and depended very strongly upon the nature of the gas. The data for nitroglycerine and PETN are as follows.

Atmosphere	O_2	Air	N_2	A
Nitroglycerine	700	800	900	2000°C
PETN	1000	1500	> 1600	> 5000°C

The evidence is conclusive. The shock alone definitely does not initiate detonation nor does it do so by heating the explosive.

Obviously, in order to heat the surface of the explosive, the gas must give off its heat to the surface. There is thus a heat exchange involved. It was pointed out by Johansson 32) that the heat exchange is not rapid enough to cause an appreciable heating unless the gas contains some solid object or particle that could be thrown against the surface. Clearly, such an object could possess no higher energy than the fallhammer, and the role of the gas bubble would not be obvious if such were the actual mechanism. Besides, it could hardly apply to the experiments by Evans and Yuill.

In view of the similarity between shock and ultrasound it is not surprising that detonation of solid explosives may be initiated by ultrasound 33, 34). This does not seem to be due to heating of the explosive. 34)

It may be added that detonation may also be initiated by friction. Sensitivity to shock and sensitivity to friction are not always parallel. Thus, barium azide is slightly sensitive to shock and extremely sensitive to friction 25), whereas pyridine perchlorate can be detonated by a hammer but not by friction. 36) The initiation by friction has been much less studied than that by shock. It should be related to the Russell effect, i.e., the formation of H_2O_2 on freshly formed metal surfaces, and the Kramer effect, i.e., the emission of electrons from freshly formed surfaces on solids.

4. EFFECTS OF THE ENVIRONMENT

It is well known that the products may accelerate the rate of decomposition of solids, and that some explosives do not detonate at all unless exposed to the products. The data on sensitivity to shock show that the initiation, prior to the appearance of the products, depends decisively upon the nature of the gas surrounding the explosive.

Apart from the evidence just referred to, there is little direct evidence as to the effect of the surrounding atmosphere on solid explosives. One important piece of evidence is the observation by Cottrell and Gibb37) that the detonation velocities of TNT and NH_4NO_3 are about 10% higher in argon than in air. According to Bowden38), nitrogen iodide covers itself with a desensitizing adsorbed layer of NH_3. If the NH_3 is removed by evacuation, explosion occurs readily. Similarly, wetting lead azide with dibutyl phthalate reduces the sensitivity and suppresses sensitization by preheating39). Morita40) reported that surface oxidation by air or O_2 of cuprous actilide increases the sensitivity to shock.

Interesting effects of metals have been reported. In Whitbread's experiments with initiation in single crystals, it was found that the maximum gap between donor and receptor with brass in the gap was 1.80 mm for aluminum, 1.55 mm for steel, 0.90 mm for RDX, and 0.15 mm for cast TNT used as reflecting witness blocks. With no witness block (air) the gap was 0.1 mm. Harlow and Skidmore22) found considerably longer initiation delays with steel than with aluminum between donor and receptor. Copp and Ubbelohde41) found a higher velocity of detonation for NH_4NO_3 encased in lead than with a steel casing.

The thermal decomposition of NH_4NO_3 and other explosives has been studied by two slightly but significantly different techniques. The conventional technique simply heats the sample. The technique developed by Schultz, Andersen, and others42) heats the sample by pressing it against a hot plate. The activation energies are different in the two cases, namely, 30-40 kcal and 7.1 kcal, respectively. It has been concluded that the gasification of the sample is the rate-determining step.43-45)

5. REACTION MECHANISMS

The decomposition of a solid into gaseous products is the rearrangement of atoms, radicals, and bonds so as to form new molecular species. For instance, the decomposition of NH_4NO_3 into NH_3 + HNO_3 requires the transfer of an H atom from the NH_4 radical to the NO_3 radical. These rearrangement processes are not well understood, but there is evidence that sheds some light on their mechanisms.

It is well known that a nitronium or a nitrosyl group in a hydrocarbon facilitates the rearrangement of hydrogen, particularly of the H atoms adjacent to this group.46) Typical of this effect is the observation that there is no exchange of H between HCl and toluene in the absence of a catalyst, and that the rate of exchange is proportional to the NO_2 pressure when NO_2 is added to the gas.47) Numerous reactions with hydrocarbons are accelerated or catalyzed by NO and NO_2.

It should be pointed out that NO_2 cannot react immediately to give nitronium. The source of nitronium is $HO{:}NO_2$, i.e., concentrated (undissociated) nitric acid. No molecule $H \cdot NO_2$ is known, and there are reasons to believe that it does not occur even as a short-lived intermediate. Nitration is therefore effected by $HO \cdot NO_2$ only. Nitrosyl, on the other hand, occurs both in $H \cdot NO$ and $HO \cdot NO$. As a consequence, HONO yields nitrites and nitrosyl compounds but no nitronium compounds.48) On the other hand, the nitration of some hydrocarbons, e.g., phenols, by $HONO_2$ is accelerated by HONO. Nitration may then occur by oxidation of the nitrosyl or nitroso compound.

The rearrangement process is of the nature of a chemical reaction with the formation of intermediate compounds with the catalyst. In particular, the catalytic effects of NO and NO_2 are caused by the formation of nitrosyl and nitronium compounds as intermediates. The mechanisms for these reactions are part of the decomposition mechanism.

There are two types of information available on the reaction mechanisms in decomposition and detonation of solid explosives, namely, qualitative observations of effects of additives and of experimental conditions in general, and quantitative rate data. Such information will be briefly reviewed in the following.

According to Braconier and Delsemme49) there is evidence that each time there has been an explosion of NH_4NO_3, there has been appearance of nitrous gases at the expense of the appearance of NH_3. Delsemme19) studied this phenomenon spectroscopically. The band systems of NO and NH_3 appear prior to explosion. The intensity of the NO bands increases more rapidly than that of the NH_3 bands but reaches a maximum two to four minutes before explosion and then decreases. The NH_3 bands increase monotonously till explosion.

These results seem to show that NO is formed from NH_3, that some other species is formed subsequently from the NO, and that the formation of this product eventually is followed by explosion of the NH_4NO_3.

Wood and Wise50) studied the effect of the HNO_3 evolved upon the explosion of NH_4NO_3. The removal of the HNO_3, e.g., by its decomposition on glass wool, reduced the rate of decomposition of the NH_4NO_3. On the other hand, Haid and Koenen51) found that HNO_3 evolved together with NH_3 in the high-temperature (above 290°) decomposition of NH_4NO_3 decomposed to form nitrogen oxides. The gas mixture was ignitable above 290° and inflamed spontaneously at about 450°C.

These results show that the product of NO just referred to may also be formed from HNO_3, and that both this product and HNO_3 are essential to the explosion.

It follows that the following reactions occur prior to explosion:

$$NH_4NO_3 \longrightarrow NH_3 + HNO_3 \qquad (1)$$

$$NH_3 \longrightarrow NO \qquad (2)$$

$$NO \longrightarrow X \qquad (3)$$

$$HNO_3 \longrightarrow X \qquad (4)$$

In order to identify X additional information is needed.

Such information is available and has been analyzed elsewhere.52,53) The first product of NO is HNO. This product may be converted into HONO. Thus,

$$NO + H \longrightarrow HNO \qquad (5)$$

$$HNO + 2\ OH \longrightarrow HONO + H_2O \qquad (6)$$

It appears that HNO, HONO, and HONNOH are required for rearrangement in condensed nitrogen compounds. The HONNOH may be formed in several ways, e.g.53,54).

$$N_2 + 2\ OH \longrightarrow HONNOH \qquad (7)$$

$$N_2O + H + OH \longrightarrow HONNOH \qquad (8)$$

HNO has been identified as a decomposition product of CH_3NO_2 and CH_3ONO.[55] The oxidation of NH_3 and the reduction of HNO_3 to HNO_2 has been observed in aqueous solutions of NH_4NO_3. The more dilute the solution, the more HNO_2 is formed.[56]

Clearly, in this mechanism several steps may conceivably be rate-determining. Since HNO is very unstable, the stabilization of the nitrosyl radical should be expected to increase the rate when the formation of HNO is not rate-determining. Halogens have this effect by forming nitrosyl halides. Accordingly, there is a catalytic effect of chloride under certain conditions.[57] If the reactions with NH_3 are rapid, those with HNO_3 may be rate-determining. In this case, addition of HNO_3 should increase the rate as observed by Wood and Wise.[50]. If, on the contrary, the reactions with NH_3 are slow, addition of HNO_3 has no effect upon the rate as observed by Guiochon.[58]

These considerations are reflected by the observed activation energies. Typical values for the decomposition of NH_4NO_3 are 6.9[59], 7.1[45, 60], 20.6[61], 21.5[62], 28.0[58], 31.4[50], 32.3[63], 36.5[58], 38.3[60], and 40.5[64] kcal. The values 20.6 and 32.3 kcal were derived from the length of the induction period. The determination of the value of 40.5 kcal was accompanied by the determination of the same value for the decomposition of ethylenediamine dinitrate.[64] Corresponding values for TNT are 27, 32, 34.4, and 46 kcal.[65] The value 32 kcal was determined from the duration of the induction period. The values 28.0 and 27 kcal and 32.3 and 32 kcal for NH_4NO_3 and TNT, respectively, are probably identical, indicating the same rate-determining step in both cases, both for the decomposition and for the induction period.

Activation energies close to those just quoted have been reported for related processes, namely as follows:

7.0 - 7.2 kcal: decomposition of $Na_2NH_4P_2O_4$[66], ortho-para H_2 conversion[67], H exchange between H_2 and H_2O[68], H_2 and NH_3[67] H_2 and N_2H_4[69], H_2 and butane[70], and H_2 and CH_4[71], desorption of H_2 from steel[72], decomposition of FeH_2[73], reaction of H_2 with Ca[74], exchange of O between O_2 and H_2O over MnO_2[75]. Rate-determining in most of these cases is the formation of OH. A typical case is the H exchange between H_2 and H_2O that is effected by the reactions[76]

$$H_2 + OH \longrightarrow H + H_2O \tag{9}$$

$$H + H_2O \longrightarrow H_2 + OH \tag{10}$$

27 - 28 kcal: decomposition of NO_2 [77], a phase transformation in NH_4NO_3 [78], equilibrium between NH_3 and H_2Se [79], reaction between NH_3 and NO_2 [80], decomposition of NH_3 on CoN [81], oxidation of CH_4 as catalyzed by NO [82], exchange between O_2 and ThO_2 [83] and between O_2 and ZnO.[84] Rate-determining is probably again the formation of OH.

31 - 32 kcal: decomposition of NH_4ClO_4 with and without addition of MnO_2 [85], of NH_3 on Mo [86], W [87], Ni [88], Re [89], Pd [90], TiN [81], FeN [81], and CrN [81], of HN_3 on glass [91], of N_2O on Pt [92,93], and of $AgNO_3$ [94], exchange between H_2 and CH_4 on Ni catalyst [95], and between O_2 and Cr_2O_3 [96], reaction of N_2 with V [97] and Ca [98], of H_2 with N_2O [99], and of CO with NO_2 [100]. Rate-determining is probably again the formation of OH. This is almost certainly the case in the reactions of N_2, H_2, CO, and N_2O, for these molecules react according to the formulas (7), (8), (9), and [101]

$$CO + 2H \longrightarrow HCHO \tag{11}$$

34.8 kcal: rearrangement of H in phenol.[102]

36 - 37 kcal: decomposition of NH_3 on W [86], synthesis of NH_3 on Fe catalyst [103], reaction of N_2 with Ti [104], exchange between O_2 and MgO.[105] These are all reactions previously associated with OH.

38 - 39 kcal: decomposition of $(NH_4)_2Cr_2O_7$ [106], tetryl [107], $(CH_3)_2CHNO_2$ [108], $EtNO_2$ [109], $EtONO_2$ [110], $C_2H_4(NO_2)CH_3$ [111], HNO_3 [112], NH_3 on W [113], Fe [114-116] and SiO_2 [117], NO_2 as catalyzed by I_2.[118] Rate-determining are probably the two reactions

$$H_2O_2 \longrightarrow 2\,OH, \quad \Delta H_0^o = 55 \text{ kcal} \tag{12}$$

$$H_2 + OH \longrightarrow H + H_2O, \quad \Delta H_0^o = -16.5 \text{ kcal} \tag{9}$$

occurring together with the results

$$H_2O_2 + H_2 \longrightarrow H_2O + H + OH, \quad \Delta H_0^o = 38.5 \text{ kcal} \tag{13}$$

40 - 41 kcal: decomposition of $(NH_4)_2Cr_2O_7$ 106), $C_2H_5NO_2$ 108), NH_3 on Pt 120), cyclonite in dicyclohexyl phthalate 121), CH_3CHO as catalyzed by N_2O 122), reaction of NO with H_2 123), and of N_2 with CaC_2. 124) Rate-determining is probably again the formation of OH, followed by reactions (5) - (8).

45.5 - 46.5 kcal: decomposition of NH_3 on Cu 125, 126), Mo 127), W 86, 128), and FeN 81), oxidation of NH_3 in a silica vessel 129), synthesis of NH_3 on W. 130) Rate-determining in these cases is probably the reaction

$$H_2O + O_3 \longrightarrow 2\ OH + O_2, \quad \Delta H_0^o = 45.5\ \text{kcal} \tag{14}$$

This reaction provides the 2OH required for the reaction of N_2 according to formula (8) in the synthesis of NH_3 on W that is a catalyst for the formation of O_3. The decomposition of NH_3 on Cu and Mo, which are also catalysts for the formation of O_3 and for the destruction of H_2O_2, should accordingly occur according to formulas

$$NH_3 + O_3 \longrightarrow HNO + H_2O_2 \tag{15}$$

and (6), followed by the heterogeneous decomposition of NH_3 with HNO and HONO by rearrangement.

The formation of OH as the rate-determining step in the decomposition of NH_4NO_3 into $NH_3 + HNO_3$ indicates the mechanism

$$NH_4NO_3 + H + OH \longrightarrow NH_4OH + HNO_3 \tag{16}$$

$$NH_4OH \longrightarrow NH_3 + H_2O \tag{17}$$

The formation of OH as the rate-determining step in the decomposition of TNT indicates reactions like

$$C_6H_2CH_3(NO_2)_3 + 2\ OH \longrightarrow C_6H_2CH_3(NO_2)_2OH + HONO_2 \tag{18}$$

$$C_6H_2CH_3(NO_2)_3 + 2\ OH \longrightarrow C_6H_2(NO_3)_3OH + CH_3OH \tag{19}$$

It is probable that HNO and HONO are instrumental in these rearrangement processes as well as in the decomposition of NH_3.

As already pointed out, the formation of gaseous NH_3 and HNO_3 from NH_4NO_3 occurs in the slow decomposition but not in the explosive decomposition. In order that the mechanisms (17) - (17) lead to explosion, it is necessary that the NH_4OH and HNO_3, if formed at all, react before desorption of NH_3 and HNO_3. This requires structural rearrangements in the solid in which NH_4OH and $HONO_2$ may be structural elements. Such rearrangements are catalyzed by HNO and HONO. Accordingly, these species, observed as NO and NO_2, are formed in the induction period. When they have reached a sufficient concentration at the surface, a state is established such that they are formed more rapidly from the decomposition than they are consumed in the rearrangement reaction. At this state decomposition occurs at increasing rate and eventually explosively.

Structural changes occurring at explosive rate are known to occur. Well-known instances are the solidification of undercooled liquids and the austenite-martensite transformation in steel and other alloys.

The evidence shows conclusively that certain species are formed in the induction period. In addition to the analyses referred to, evidence is available to the effect that certain additives shorten the induction period or suppress it altogether. This has been observed with liquid TNT. 65) In this case, addition of decomposition products (unfortunately not identified) completely removed the induction period. Previous exposure to ultraviolet light had the same effect. Several additions, particularly NH_3, increased the rate of decomposition and shortened the induction period. It may be mentioned in this connection that NH_3 is a product of oxidation and hydrolysis of N-containing substances.

6. CONCLUSION

The evidence and arguments presented in the preceding sections strongly indicate a role in the initiation mechanism of such species as are formed by shock in air. These species are primarily H and OH and secondarily HNO and HONO. These are known to catalyze rearrangement in condensed hydrocarbons.

The evidence is not claimed to show that this is the only effect of the shock. It is clear that some of the reactions would be accelerated by the heat conveyed by the shock.

In order to make the evidence conclusive, additional experimental study is required. Such study should include the chemistry of shock and friction and the chemistry of explosives. The former study could well be pursued with the use of any convenient explosive, e.g., NH_4NO_3, as an indicator. The latter study must necessarily use explosives of actual interest. It is then important that the shock conditions are known and controlled.

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APPENDIX B

AEROJET-GENERAL CORPORATION
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INITIATION OF EXPLOSIVES BY FRICTION

by

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ABSTRACT

Experiments have been conducted aiming at identification of the pertinent variables in the initiation of explosives by friction. Nitrogen iodide was initiated by touching it with various metals and alloys and with glass and also by exposure to fumes from nitric acid decomposed by stannous chloride and to drops of acids. Hydrogen peroxide gave violent decomposition but no detonation. Ammonia inhibits detonation. The sensitivity to touch was highest with aluminum and copper, lowest with stainless steel and glass. Detonation was preceded by an induction period. The sensitivity increased with repeated touching. It is concluded that initiation is effected by reactions with the atmosphere on the new surfaces formed in fracture and abrasion. The mechanism of initiation by friction is similar to that for the initiation by other means, e.g., impact, shock, and electric discharge.

1. INTRODUCTION

A major problem in the study of the sensitivity of propellants and explosives to initiation by friction is the identification of pertinent variables. Unless this problem is adequately solved, neither fundamental research nor technological testing in this field can be undertaken. Exploratory experiments in this direction will be reported in the following. These have been designed to supplement information given in the literature. A review of the literature is given in Section 2.

The conspicuous effects of friction upon an explosive powder are abrasion, fracturing, and heating of the grains. The fracturing itself, under conditions of no abrasion or heating, initiates certain sensitive explosives, such as lead azide, provided the grains are large enough. Heating the explosive in the air in the absence of abrasion and fracture may also cause initiation. The effect of abrasion alone is hard to study with anything but the largest crystals that are unsafe, if sensitive at all, and no information on this effect seems to be available.

In addition, the sensitivity of the explosive depends upon the material against which it is rubbed, e. g. , fiber, wood, or steel in the shoe of the friction pendulum.

As to the explosive itself, there are drastic effects of moisture and grain size in addition to the obvious effect of chemical composition.

The composition of the surrounding atmosphere has attracted little interest in the past. The moisture content of the explosive powder is clearly related to the humidity of the air. Our experiments have shown decisive effects of the atmosphere. It seems to be possible to initiate certain explosives by merely exposing them to a suitable atmosphere. This effect is of particular technological importance since the explosive may create its own atmosphere by its slow decomposition in storage.

An inherent difficulty in the study of the initiation by friction is the definition of friction. This definition depends entirely upon which of the effects of friction is considered essential. Thus, if initiation occurs by fracture, no sliding motion, merely pressure, is required for initiation. In this case, relative velocity is irrelevant. Furthermore, when comparing different explosives, pressure alone is an inadequate measure of sensitivity since different pressures may be required for fracturing the grains in the different explosives.

The mechanism of initiation by friction is closely related to that of initiation by impact and shock. The mechanism of initiation with emphasis upon initiation by shock was treated in a preceding report[1)]. It was concluded that initiation is effected by certain chemical reactants, primarily H, OH, NO, and NO_2, that are formed by shock in air. This conclusion is borne out by our experiments with initiation by friction.

It follows from this discussion that initiation by friction is hardly distinguishable from initiation by other means, both as to basic mechanism and practical implications. Experiments with initiation by impact and by shock are planned in other investigations, and it is expected that the results will be applicable to the initiation by friction. In view of this situation it has been deemed proper to limit the study of initiation by friction to its peculiar features as compared to initiation by impact or shock.

2. REVIEW OF THE LITERATURE

Whereas the sensitivity of an explosive to impact and shock may be quantitatively expressed by means of the dropweight and cardgap tests, there is no quantitative test for the sensitivity to friction. The friction pendulum does not seem to give quantitative data of a reliability comparable to those given by the other two tests.

Tomlinson2), in his compilation of data on explosives, does not express sensitivity to friction by numbers but rather by descriptive terms such as "unaffected", "explodes", "crackles". An exception is lead azide, the sensitivity of which seems to fall right into the range of the friction pendulum. In this case, Tomlinson gives the number of cases of initiation and no initiation in a series of tests with fiber shoe and steel shoe at various moisture contents. It appears that the steel shoe gives a higher sensitivity than the fiber shoe. Howell3) also found that a steel shoe gives a higher sensitivity than a wood shoe.

In spite of the qualitative nature of the classification of the sensitivity of explosives to friction, as insensitive, sensitive, and very sensitive, the evidence available is informative on some essential points.

One might expect that sensitivity to friction is parallel by sensitivity to impact. Such is indeed the rule, but there are noteworthy exceptions. Thus, pure pyridine perchlorate is sensitive to impact but not to friction4), barium azide5-7) and lead dinitro resorcinate6) are slightly sensitive to shock but extremely sensitive to friction.

There are two main differences between friction and impact that may be related to a difference between the two with respect to initiation. One difference is that impact causes shock in the air. This has been found to be decisive to the initiation by impact. The literature on this subject was reviewed in a preceding report1). Another difference is that impact occurs once only, whereas friction causes repeated alternating loading and unloading. Our experiments show that this latter effect is significant. This effect is similar to the so-called memory effect in thermal initiation, according to which the induction period at a given temperature has the same duration at intermittent as at continuous holding at temperature8-11).

Some explosives, e.g., lead azide, silver azide, cyanuric triazide, may be initiated by fracture of single grains7). This effect increases with the size of the grains. The explosives just mentioned are comparatively insensitive to friction when they contain small particles only. One reason for this grain-size effect is that small grains are not easily broken. Another reason is that the new surface formed in the fracture of a larger grain has a larger area with a correspondingly larger amount of surface reaction products.

The formation of new surfaces in abrasion and fracture is accompanied by emission of light. This phenomenon, known as triboluminescence, has been studied with a variety of organic and inorganic solids. The spectrum consists of a continuum and a band structure. The bands are some of those characteristic of N_2, NO, and H_2O or OH12-14). They are absent when the sample is held in a vacuum15). The site of the glow is the air up to a centimeter or so above the solid14). The luminescence shows that chemical reactions occur on and at the new surfaces, notably the oxidation of N_2 to NO and subsequent photochemical reactions of NO. A product of the reactions of NO is presumably NO_2.

These observations bear directly upon the initiation of explosives by fracture of grains. It is known that a mixture of NO, NO_2, and H_2O reduces the induction period in the thermal initiation of nitroglycerin to zero16). It appears that NO and NO_2 are instrumental in the thermal initiation of ammonium nitrate17-21). In our experiments, nitrogen iodide detonated immediately upon contact with the brown fumes from the decomposition of nitric acid with stannous chloride.

Closely related to these phenomena is the Russel effect, the formation of hydrogen peroxide on new surfaces of metals caused by plastic or elastic deformation, abrasion, and fracture. This effect would be expected to be particularly important in the initiation of explosives based on hydrazine, ammonia, and hydrazoic acid, such as hydrazine perchlorate, ammonium nitrate, and the azides22, 23). Some metals, e.g., Al and Zn, do not decompose hydrogen peroxide, other metals, e.g., Cu and Fe, do. Accordingly, different metals should be expected to be differently effective in the initiation by friction. That such is the case follows from the effect of the shoe material in the friction pendulum, just referred to, from the results of Bowden et al24), and from our experiments with different metals and alloys. It should be pointed out that the hydrogen peroxide is formed in reactions with the environment, e.g., the ordinary (moist) air and aerated water. The dependence of sensitivity upon the metal should therefore be related to the composition of the atmosphere. The information available is inadequate for correlating the Russel effect, including nature of metal and composition of atmosphere, with the sensitivity of explosives to friction. Further investigations in this important area are needed.

The initiation of various explosives by friction against various metals has been studied by Bowden et al24). A rotating disk was smeared with the explosive in a thin layer against which a slider was pressed. The amount of friction was expressed in terms of velocity of the disk and force applied to the slider. At a fixed velocity of the disk, the force on the slider was increased until the explosive was initiated. This force was plotted against the thermal conductivity of the metal of which the slider was made. The plot is roughly parabolic, force proportional to square root of thermal conductivity. The metals used in this plot were constantan (60% Cu, 40% Ni), nickel, steel, and tungsten. A similar plot was obtained when the appearance of hot spots was taken as indication instead of initiation. It was concluded that initiation was caused by heating the explosive, and that metals of higher thermal conductivity conduct away the heat more rapidly and thereby reduce the temperature as compared to metals of lower thermal conductivity.

The choice of slider material in this experiment was not well designed to prove the point. The metals of extreme thermal conductivities, silver, copper, and aluminum at one end and stainless steel at the other end, were not among those used. Nor was a comparison made with poor thermal conductors like glass or wood. The results are opposite to those obtained with the friction pendulum using wood or fiber shoe as compared to steel shoe. Our experiments show that poor thermal conductors (glass, stainless steel) may give less sensitivity to friction than good thermal conductors (copper, aluminum). Furthermore, the force on the slider as such does not define the rate of heat supply that is determined by the friction force. Accordingly, there should be a noticeable effect of surface roughness of the metal. There is no such effect. On the other hand, it is doubtful whether the apparatus is anything but a crude heating device, and whether the experiment pertains at all to initiation by friction.

It may be mentioned in this connection that temperature is not the decisive factor in initiation of explosives. Data showing this point were quoted in the preceding report1). To those may be added the following values given by Scott, Jones and Lewis22) for the ignition temperature of hydrazine on different supports and in different atmospheres.

Ignition Temperature, °C

Support	In Air	In O_2	In N_2
Pyrex glass	270	204	-
Platinum	226	30	-
Fe_2O_3	23	-	23
Black Iron	132	-	131
Stainless Steel	160	-	> 415 (no ignition)

When explosives have several crystallographic modifications, the different phases show different sensitivities to initiation. This applies to the initiation of lead azide by friction6, 7) and to the initiation of ammonium nitrate by shock or impact25). The effect of friction upon the phase transformations of explosives has apparently not been studied, but comminution is known to effect phase transformations in various compounds, e.g., zinc sulfide26-30) and calcium carbonate31). It is therefore conceivable that fracture of the grains of an explosive may cause the conversion of the grains into a more sensitive modification. The reason why the sensitivity depends upon the crystallographic form falls beside the scope of this report. It may be mentioned, however, that the different modifications may contain different amounts of some impurity. Thus, preliminary results with ammonium nitrate indicate a change in water content at the transition at 84°C32).

A desensitizing effect of moisture has been found with several explosives, e.g., lead azide and nitrogen iodide. Accordingly, the moisture surface of a grain is insensitive, whereas the dry surface suddenly exposed upon fracture is sensitive. On the other hand, decomposition and thereby initiation requires the presence of water in many cases. Thus, water is instrumental in the decomposition of ammonium nitrate21, 33). The moisture content of the explosive is related to the humidity of the air, and there is thus at least this effect of the composition of the atmosphere upon the initiation. Other atmospheres than air have apparently not been tried in studies of initiation by friction.

3. EXPERIMENTAL

The evidence presented in Section 2 bears out the need for experimental study of the basic principles involved in the initiation by friction. While ignorant of those principles one could hardly design a meaningful test of sensitivity of explosives to friction. It should be emphasized in this connection that the ultimate objective of this investigation is primarily the testing of propellants as to sensitivity to friction, and secondarily the improvement of materials and procedures with respect to safety in manufacture, handling, and storage. The study of the mechanism of initiation should then be pursued to the extent called for by these objectives and no further. Experiments have been designed on these premises and with a view to supplementing information already available.

To the purpose at hand the choice of explosive is one of convenience alone. The explosive should be sensitive enough to be set off by hand and by a light enough touch to be controlled, reproduced, and watched. It should be simple to make, since the requirement on sensitivity is prohibitive to transportation. It should be safe in handling. These requirements are ideally met by nitrogen iodide. This explosive was used exclusively in the experiments reported in this section.

The nitrogen iodide was produced from concentrated ammonium hydroxide and solid iodine. The reaction was completed in about 30 minutes. The product probably has the composition $NI_3 \cdot nNH_3$ with an unknown number n of NH_3 groups in the complex. This product was filtered on filter paper and washed with water. Thorough washing gave an extremely sensitive product, and the washing was therefore made incomplete. Immediately upon washing, the product was divided into small lots, of an estimated weight of the order of a milligram. One batch gave roughly 40 small samples. These were placed on small pieces of filter paper, about one inch square, and were set on a table to dry in the ambient for 30 minutes.

The samples thus produced had a suitable sensitivity and were well enough reproducible for the purpose at hand. However, they lost sensitivity with time and could hardly be used for more than an hour after the drying period. The samples had an appearance of dryness immediately after drying, but after aging they looked moist and smeared onto metals. The NH_3 of the complex is known to reduce the sensitivity, and it is probable that the loss of sensitivity through aging was caused by a surface coat of NH_3[34]. As an indication of the sensitivity immediately after drying it may be mentioned that a sample was initiated by dropping it on the table from a height of about 6 inches. Sympathetic initiation occurred at a distance of about 4 inches between the samples. The aging did not appreciably reduce the sensitivity of the material to shock.

It appeared that the particle size affected the sensitivity. When the iodine particles were used as taken out of the reagent bottle, the particle size of the explosive appeared to be greater than when the iodine particles were crushed. The samples prepared without crushing the iodine were more sensitive and more reproducible.

The samples were initiated by touching them with pieces of sheet metal or with a glass rod. The metals were Cu, Al+ 3% Cu, and stainless steel (18/8). There were noticeable differences between Al alloy, the stainless steel, and the glass, the sensitivity decreasing in that order. Cu gave about the same sensitivity as the Al alloy, possibly slightly less. The differences showed up clearly in the amount of force required for initiation while pressing the metal against the sample. Other metals were tried, various steels and various Al alloys, but the differences were not great enough to permit their rating in terms of relative sensitivity.

The metals were tried as received and after cleaning the surface with a file. There was no noticeable effect of the state of the surface or of its roughness.

An attempt was made at a quantitative classification of the metals according to sensitivity in terms of numbers of go - no go at a "standard touch". This method did not work out as well as expected owing to the spread in the sensitivity of the samples. It was well possible to apply a touch that always initiated with aluminum and never with stainless steel, but this test did not permit a sharper distinction than did the feel of the touch.

Samples of intermediate sensitivity showed an induction period and went off after some time under constant pressure. Slightly less sensitive samples, that did not go off while pressure was applied, went off when the pressure was eased. At still lower sensitivity, the samples went off at a second, third, or fourth try. Initiation then frequently occurred at the very slightest touch. This shows that the prior application of pressure caused sensitization of the sample.

The decomposition products of NI_3, being N_2 and I_2, its decomposition should be promoted by NO + NO_2 and also by H_2O_2. Nitric acid was decomposed by stannous chloride, and the fumes of NO + NO_2 were conducted through a glass tube with a small orifice to a sample of NI_3. When the fumes reached the sample, it detonated immediately. The fumes were moist, but the usual desensitizing effect of moisture did not show up under these conditions. Thus, in an atmosphere containing these fumes, the sensitivity is so great that no friction at all is required for initiation. As a check, a sample was exposed to a draft of air that was gradually increased until the sample blew away. There was no initiation in this experiment. It may be mentioned in this connection that detonation or violent decomposition also occurred upon addition of a drop of concentrated nitric acid, sulfuric acid, or hydrochloric acid to the sample.

When 30% H_2O_2 was added to NI_3, the reaction was violent with rapid evolution of gas of the color of the gaseous detonation products. Even with extremely sensitive samples, addition of H_2O_2 did not cause detonation. The gas was probably I_2. The treatment with H_2O_2 was used for disposal of surplus samples and the residue on the filter paper. When stainless steel was wetted with 30% H_2O_2, it initiated the NI_3 at the slightest touch.

Although there was no noticeable effect of surface roughness, the samples detonated much more readily when touched with the edge of the metal than when touched with the flat surface. It appeared that breaking or cutting of grains gave by far the most effective initiation. On the other hand, the sensitization by repeated touching was apparently not associated with the breaking or cutting of grains but rather with abrasion. Thus, an insensitive sample could be spared over the filter paper and the grains rolled back and fourth over the filter paper until the sample suddenly detonated.

4. THE MECHANISM OF INITIATION

The information gathered from the simple experiments reported in Section 3 supplements the information in the literature on a few important points. It is well consistent with the mechanism derived previously for the initiation by shock1). The information obtained does not permit the identification of the details of the mechanism for the initiation by friction, but it does indicate its basic features.

The use of NI_3 in these experiments is fortunate in the respect that a wide range of sensitivity could be studied. This is more to the point at hand than the study of a large number of explosives. The results are therefore more general than might at first sight appear.

The initiation by friction is associated with an induction period, the duration of which is inversely related to the sensitivity of the explosive. The induction period shows the same characteristics as those encountered in thermal initiation and shock initiation: it is shortened or suppressed by the addition of certain reactants, such as $NO + NO_2 + H_2O$, and it shows the memory effect. One may then safely assume that the phenomena occurring in the induction period are identical in all these cases of initiation. Consequently, this particular feature of the initiation mechanism can be studied under simpler experimental conditions than in friction experiments, notably in thermal initiation.

The part of the initiation mechanism that is peculiar to friction is then the initiation of the induction period phenomena. The fact that $NO + NO_2 + H_2O$ suppresses the induction period shows that these species themselves, or some other species that are rapidly formed from them, cause detonation. The distinction between the two alternatives is rather subtle and of minor technical significance. It appears, however, that the hydration and hydrogenation products, HNO, HON, HONO, and $HONO_2$, are the effective species. The same species, i.e., NO, NO_2, H, and OH, are formed on new surfaces resulting from abrasion and fracture of solids in air, and the same species are also formed by shock in air. It seems then to follow quite unambiguously that the essence of the initiation by friction as well as by shock is the formation of these initiating species.

In both cases, shock and friction, the NO is formed by oxidation of N_2. This requires the presence of N_2 and an oxidizing agent, as in air. Accordingly, the initiating species are formed in greater abundance when the air has unrestricted access to the new surfaces formed in friction. Hence, detonation may occur when the pressure on the sample is released, or when the sample is alternatingly exposed to pressure and air.

In this mechanism, the role of the metal rubbed against the explosive is secondary. However, if the supply of H or OH is rate-determining, the new surface of the metal may supply sites for the decomposition of H_2O into H + OH. Such metals as Al and Zn, that catalyze the formation of H_2O_2 but not the decomposition of H_2O_2, would then be particularly effective by forming H_2O_2 or pairs of OH. Other catalytic effects of the metal may be in the formation of O_3, either from NO or from H_2O_2, notably when O_3 is an essential reactant. Such seems to be the case when NH_3 is a product of the explosive because O_3 reacts with NH_3 to form H_2O_2 and HNO[35],

$$NH_3 + O_3 \longrightarrow HNO + H_2O_2 \qquad (1)$$

Catalysts for the formation of O_3 are such metals as Cu and Ag. When H_2O_2 is decomposed into O_2 and H_2O, it is merely destroyed and cannot take part in the initiating reactions. A catalyst for this type decomposition of H_2O_2 is Fe, and steel should therefore inhibit initiation rather than promote it. All this is fairly in accord with the observed effects of metals. It should be borne in mind, however, that the reactions catalyzed by the metal may not affect the rate-determining step, and that several competing reactions are involved. Generalization of the effect of the metal should therefore be done with some caution. In particular, the catalytic effects of metals are frequently different in acidic and basic environments and under oxidizing and reducing conditions.

The mechanism outlined above is general to the extent that NO + NO_2 + H_2O effects detonation or initiation. This applies to several common explosives and propellants, e.g., NH_4NO_3, nitroglycerin, and TNT. Hydrazine compounds probably belong to this group. Again a word of caution is in order. The supply of these reactants may not suffice in a specific case if they are destroyed by some competing reaction, e.g., by an inhibitor, faster than they are supplied.

The reaction mechanism for the decomposition of NI_3 into N_2 and I_2 is comparatively simple. The formation of I_2 probably occurs by the same mechanism as the formation of Cl_2 from NaCl,

$$NaCl + H_2O_2 \rightarrow NaOH + HOCl \tag{2}$$

$$NaCl + H_2O \rightarrow NaOH + HCl \tag{3}$$

$$HCl + HOCl \rightarrow Cl_2 + H_2O \tag{4}$$

The formation of N_2 occurs by the reaction36)

$$HON + HN \rightarrow N_2 + H_2O \tag{5}$$

These reactions do not apply to all explosives but they are representative of the type of reactions that are effective in initiation of most explosives.

Some of the reactions in the general initiation mechanism are accelerated, some decelerated, when the temperature is increased. It is by no means obvious that initiation by friction or by other means is invariably promoted by a high temperature. Some of the reactions, notably the oxidation of NO37-40), are actually inhibited by heating, owing to the instability of intermediate compounds. The oxidation of NO occurs via HNO, 36)

$$H{\cdot}NO + HO{\cdot}NO_2 \rightarrow N_2O_3 + H_2O \tag{6}$$

This process may be inhibited by the rapid decomposition of HNO into H_2 and NO or by the formation of comparatively stable ClNO. It may also be accelerated by the formation of ClNO that preserves the NO radical. The latter case seems to apply to the decomposition of NH_4NO_3 in the presence of NH_4Cl[41, 42]. The stabilization of HNO at low temperatures may explain the increased sensitivity of certain primary explosives at liquid nitrogen temperature[43].

5. CONCLUSION

A few important conclusions may be drawn from the evidence presented in Sections 2 and 3 and from the mechanism outlined in Section 4.

In technical applications the important question is not to what degree an explosive or a propellant is sensitive to initiation by friction, but under what conditions it is sensitive or insensitive to initiation.

In technical applications it is hard to visualize a case of friction clearly distinguished from crushing or impact. It follows from the evidence and arguments presented that such a distinction lacks a meaning. No useful purpose could be served by a test that purports to simulate a construed case of friction. It appears that a hazard may be created by labeling an explosive as insensitive to friction or as sensitive to friction only, friction being arbitrarily defined.

The observations reported in Section 3 bring out the similarity between initiation by friction and initiation by other means, e.g., shock, impact, thermal initiation. The initiation by friction is associated with an induction period and shows the memory effect that is characteristic of the induction period. The initiation by friction depends upon the material rubbing against the explosive. Although there is no direct relation between sensitivity of the explosive and heat conduction of the material in contact with the explosive, the greater sensitivity with copper and aluminum as compared with stainless steel and glass shows that the heat generated in friction is not a decisive factor. As in initiation by other means there is a conspicuous effect of the composition of the surrounding atmosphere upon the sensitivity of the explosive.

Initiation by friction occurs by the same mechanism and, indeed, by the same means as initiation by shock, impact, etc. It seems therefore logical to investigate the simpler cases of initiation first and to apply the knowledge gained to the composite case of friction at a later stage.

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APPENDIX C

The Effect of ϵ -Carbide on the Passivity of Steel in Nitric Acid Solutions.

by

T. G. Owe Berg

Summary

Carbon steels of 0.10% C, and 0.95% C were heat treated to produce ferrite + cementite, martensite, and martensite tempered at 200° C. Specimens were immersed in nitric acid solutions of various concentrations and the minimum concentration required for passivation was determined. This concentration depends upon the amount of hydrogen-rich phase, ϵ -carbide, in the specimen. Steel containing ferrite + cementite alone is passivated by 7.2 N acid, steel containing tempered martensite at a higher concentration, and steel containing untempered martensite at a still higher concentration. The results are related to other observations with dissolution and etching of steel in nitric acid and with ϵ -carbide.

1. INTRODUCTION

The various phases in steel are attacked at different rates by certain etchants. Etching therefore gives a pattern to the etched steel surface according to size, shape, and distribution of such phase particles as are distinguished by the etchant.

The fact that different phases react chemically at different rates indicates that they have different chemical compositions. Hence, etching may be employed to show the presence of phases of known compositions and to determine the composition of phases known to be present.

The ideal etchant is one that attacks the phase or phases under study or at these phases while the matrix itself is passive to the etchant. The art of etching centers on the selection of such etchants. A particularly interesting etchant for steel is concentrated nitric acid, towards which ferrite, sustenite, and cementite are passive while certain other phases are not.

This paper reports on experimental studies of passivity and activity of various phases in steel towards nitric acid.

2. REACTIONS OF STEEL WITH NITRIC ACID

The mechanism of reaction of Fe with aqueous HNO_3 has been derived from rate measurements elsewhere1).

Armco iron and carbon steel are passive, i. e., dissolve very slowly, in concentrated nitric acid. The passive state is preceded by a period of dissolution, the duration of which seems to depend upon the prior treatment of the steel. With Armco iron and annealed carbon steel, passivity occurs above 7. 16 N. At this concentration, the degree of dissociation is $\alpha = 2/3$, i. e., the concentration of dissociated HNO_3 is twice that of undissociated HNO_3.

The passivation of iron and steel in HNO_3 solutions is caused by adsorbed NO_2, nitronium, according to the formula

$$HONO_{2\ ads} \longrightarrow OH_{ads} + NO_{2\ ads}$$

The $NO_{2\ ads}$ is decomposed to NO, nitrosyl, by certain metals, e.g., Cu, but not by other metals, e.g., Fe. For this reason, Cu dissolves rapidly in concentrated HNO_3 and at a rate proportional to the concentration of undissociated $HNO_3$1). For the same reason, Fe is passivated by undissociated HNO_3. The decomposition of $NO_{2\ ads}$ to NO_{ads} by some agent present with the Fe would cause the formation of nitrosyl compounds of Fe and thereby the dissolution of the Fe. Such agents are certain carbons and carbides2). Other carbides, including cementite, do not effect decomposition of $NO_{2\ ads}$ and therefore do not affect the passivity of the Fe.

The reduction of NO_2 to NO is effected by atomic hydrogen. There are reasons to believe that carbons and carbides decompose NO_2 by means of the H they contain. An H-bearing carbide destroys passivity in concentrated HNO_3, whereas an H-free carbide does not. H dissolved in Fe would have the same effect, and H-bearing Fe therefore dissolves in concentrated HNO_3 until the H concentration has been reduced sufficiently. This occurs in the period of dissolution preceding passivity. But if an H-bearing carbide is present, the H may not be removed from the carbide but continue to decompose the HNO_3 by a catalytic effect. The reaction mechanism may then be as follows

$$HO\cdot NO_{2\ ads} \longrightarrow OH_{ads} + NO_{2\ ads}$$

$$NO_{2\ ads} + H_{carbide} \longrightarrow NO_{ads} + OH_{ads}$$

$$H\cdot ONO_{2\ ads} \longrightarrow H_{carbide} + NO_{3\ ads}$$

with the net result

$$HO\cdot NO_{2\ ads} + H\cdot ONO_{2\ ads} \longrightarrow 2OH_{ads} + NO_{ads} + NO_{3\ ads}$$

Thus, one undissociated and one dissociated HNO_3 molecule give together the formation of hydroxide, nitrosyl, and nitrate which are all soluble. The H-bearing carbide may thus cause continuous dissolution of the adjacent Fe without being attacked itself.

The H-bearing carbide of Fe is the ϵ-carbide. This carbide has been prepared and analyzed with respect to H. It contains much H, and its composition is probably Fe_2HC3). Dissolution of steel in concentrated HNO_3 is thus indicative of presence of ϵ-carbide in the steel. Attack of steel by concentrated HNO_3 at grain boundaries is indicative of presence of ϵ -carbide in the grain boundary material. Etching with concentrated HNO_3 is accordingly a means of detecting ϵ -carbide in steel.

Essential in this reaction mechanism is the NO_2 group of the undissociated HNO_3. The same group occurs in picric acid that is frequently used as an etchant, its composition being $(NO_2)_3C_6H_2OH$. Consequently, picric acid may also be used for detecting ϵ -carbide in steel.

In addition to these etchants, there are other acids, particularly organic acids, which require H for their reaction with Fe, e.g., for the reduction to CO and formation of carbonyl. A discussion of the reaction mechanisms of these acids would carry beyond the scope of this paper.

3. EXPERIMENTAL

Carbon steels of types 1010, 1018, and 1095 were available in sheets of approximately 1 mm thickness. Specimens were cut from these sheets, approximately 5 mm by 35 mm, and heat treated so as to produce diferent structures with different amounts of ϵ -carbide. The carbon contents of these steels are 0.10%, 0.18%, and 0.95%, respectively. The 1010 and 1018 steels were austenitized in argon at 930°C for 1/2 hr, the 1095 steel at 870°C for 1/2 hr, and then water-quenched. This treatment was designed to produce a martensitic structure. One lot was then tempered in argon at about 200°C for 2 hr and then air-quenched. This treatment was designed to produce a tempered martensite that is known to contain ϵ -carbide. Another lot was tempered in argon at 680°C for 2 hr and then air-quenched. This treatment was designed to produce ferrite + cementite free of other phases. Prior to heat treatment, a small hole was drilled at one end of each specimen so that it could be suspended in a Saran thread through the hole.

The heat treated specimens were suspended in nitric acid solutions of various concentrations in open beakers and without stirring. Specimens containing no hydrogen-rich phase should then be passivated by nitric acid above 7.16 N[1,4]. Specimens containing ϵ -carbide should, according to the mechanism outlined in Section 2, require a higher concentration of nitric acid for their passivation, depending upon the amount of ϵ -carbide present. The concentration required by each specimen for passivation to occur was determined to ± 0.05 N, the accuracy of this determination being limited by the error of titration. Passivity occurred within 20 sec or not at all, depending upon the heat treatment of the specimen and the concentration of the acid.

It is essential to the accurate determination of the concentration required for passivation that the specimen be initially in the active state. The specimen should therefore be immersed in an acid solution below this concentration first and the limit be approached from the low-concentration side. This is particularly important if the specimen has been surface decarburized, e.g., by heating in air. The passivated specimen can be depassivated by exposure to the air or, more quickly, by wiping it on a towel or by scratching its surface.

The accuracy of the determination of the passivity limit was in this experiment that of titration. Actually, the limit between passivation and nonpassivation is much sharper. Thus, it was frequently possible to distinguish between a fresh solution and a solution that had been used once before and thereby slightly depleted. The reproducibility was good to this accuracy, both with one specimen after repeated passivations and depassivations and with several specimens from the same lot. Somewhat surprising is that specimens of type 1095 steel heat treated on different occasions to give a martensitic structure, one in argon and one in air, gave the same concentration limit within the accuracy of titration. The specimens heat treated in air were surface decarburized and therefore required to have a thin surface layer removed by abrasion or by dissolution in low-concentration nitric acid in order to yield the same result as the specimens treated in argon.

Table 1. Lowest normality of nitric acid at which passivation occurred.

	1010	1018	1095
Ferrite + cementite	7.2	7.2	7.5
Tempered martensite	7.3	8.0	10.0
Martensite	7.6	8.6	14.2

The "ferrite + cementite" specimens of 1010 and 1095 did not become passive in less than 7.4 N and 7.5 N acid, respectively, when treated as just described. This indicates that they contain some ϵ-carbide. The specimens called "cementite + ferrite" and "martensite" were therefore tempered at 260-270°C for 20 hr. After this treatment all these specimens of the 1010 and 1018 steels were passivated by 7.2 N acid.

The martensite specimens of the 1095 steel were analyzed for hydrogen by the combustion technique, using the LECO instrument for the determination of hydrogen in titanium and zirconium metals. These specimens were nearly completely martensitic. The hardness was 64 RC. Two specimens weighing 1.5720 and 1.5250 g, burned to give 1.6 and 1.3 mg of water, corresponding to 0.011 and 0.010 weight percent of hydrogen, respectively. These are comparatively high contents of hydrogen, about 100 ppm, whereas annealed steel contains of the order of 2-4 ppm. Such small amounts cannot be determined by this method of analysis. But even 100 ppm is little for a hydrogen-rich phase of stoichiometric composition. Multiplying the analysis values by 12 gives the corresponding carbon concentrations 0.14 and 0.12%, respectively. Thus, there is one H atom for every 7 or 8 C atoms.

4. DISCUSSION

The results in Table 2 show drastic differences between the different heat treatments. At a given carbon content, "martensite" requires a much higher concentration for passivation then does "ferrite + cementite"; "tempered martensite" falls between these limits. This concentration increases with the carbon content of "martensite" and "tempered martensite" and is independent of the carbon content for "ferrite + cementite".

Tempered martensite is known to contain ϵ -carbide[5-15]. ϵ -carbide is known to contain hydrogen[3]. Hence, tempered martensite should require a higher concentration of nitric acid for passivation that does ferrite + cementite. This is in agreement with observation. But untempered martensitic specimens require still higher concentrations of nitric acid for passivation. Hence, they should contain still more hydrogen.

It may be concluded from the analysis for hydrogen in the martensitic 1095 steel that martensite does not contain hydrogen in a stoichiometric ratio, i.e., martensite is not a hydrogen-rich phase, although it may contain some dissolved hydrogen. Instead, it must be concluded, most of the hydrogen was held as ϵ -carbide. Accordingly, about 14% of the carbon in these specimens should occur as ϵ -carbide.

Hydrogen dissolved in martensite could hardly affect the passivity any more than hydrogen dissolved in ferrite. The dissolved hydrogen, whether in martensite or in ferrite, is desorbed in the active period preceding passivation. In order drastically to affect passivation, the hydrogen must be held in a hydrogen-rich phase, e.g., ε-carbide. But a hydrogen-rich phase, as distinguished from a phase holding hydrogen in solid solution, contains hydrogen in a certain stoichiometric ratio, and martensite does not. It follows that martensitic steel, whether tempered or not, contains ε-carbide, i.e., martensite is partly transformed into ε-carbide, whether tempered or not. The results in Table 2 show then that untempered martensitic steel contains more ε-carbide than does tempered martensitic steel. It should be emphasized that this conclusion pertains to the specimens used in this investigation.

Tempering of martensite at and below 175°C produces changes in various properties. The magnetic intensity decreases[9,16]. This decrease is rapid during the first few minutes and then reaches a level that depends upon the the carbon content but varies little with the temperature[9]. The c/a ratio of the martensite decreases, indicating a loss of carbon[17]. The electron microscope reveals a mottled structure after tempering at 100°C for 5 hr[5]. Carbide particles have been extracted from martensite tempered at 150°C for 170 hr. They consist of cementite; no ε-carbide was found with this technique[18]. After tempering above 175°C, a network of carbide has been observed at grain and subgrain boundaries[5,6]. ε-carbide has been identified by X-ray diffraction in specimens tempered at about 200°C[5,6,10,11].

The evidence referred to is compatible with the conclusion drawn from the results of the present investigation, namely, that both untempered and tempered martensitic steel contains ε-carbide, and that tempering converts this ε-carbide partly into cementite.

It follows from the results of this investigation and the evidence referred to that martensitic steel produced by quenching from austenite contains ε-carbide in fine dispersion with a particle size too small for observation and identification by conventional techniques, e.g., electron microscopy and X-ray diffraction. Whether such martensite is invariably accompanied by ε-carbide will be the subject of a separate investigation. The observations made in the present investigation are not conclusive on this point. It also follows that tempering of such martensitic steel produces larger particles of ε-carbide, tending to agglomerate at grain and subgrain boundaries, and also causes the ε-carbide to convert partly into cementite.

5. APPLICATIONS

The determination of the concentration of nitric acid required for the passivation of steel is a very sensitive method for the detection and identification of ϵ -carbide. In addition, it is simple, rapid, and convenient. It supplements conventional techniques by responding to ϵ -carbide in fine dispersion. There is a quantitative relation between the concentration of nitric acid required for passivation and the amount of ϵ -carbide present. This technique will be used in further studies of ϵ -carbide in steel to be reported later. Preliminary tests indicate that it is also applicable to detection and identification of the corresponding hydrogen-rich carbide of nickel. A few other applications of the reaction mechanism outlined in Section 2 and the role of ϵ -carbide in this mechanism will be briefly mentioned.

a. Etching by Nitric Acid.

Since ϵ -carbide is an intermediate product in the formation of other carbides, ϵ -carbide should be expected to occur at the boundary between carbide precipitates and the matrix. This ϵ -carbide should then cause attack by the acid at this boundary. Sensitized stainless steel is attacked at grain boundaries such that a groove is eaten in the grain adjacent to the grain boundary. This attack indicates the presence of ϵ -carbide.

b. Temper Brittleness.

Etching with picric acid reveals grain boundaries and subgrain boundaries in temper-embrittled but not in unembrittled steel19-21). The embrittled steel is attacked at the grain boundaries of the primary austenite, which form the subgrain boundaries in the ferrite or martensite, and also at the ferrite grain boundaries. Addition of Nb suppresses temper brittleness and also this etch effect21).

There is thus a correlation between temper brittleness and the etch effect and, thereby, ϵ -carbide. There are numerous observations to this effect. Thus, the susceptibility to temper brittleness increases with the carbon content20,22). The embrittlement occurs in the early stage of the transformation of martensite23). This is the stage in which ϵ -carbide appears at grain and subgrain boundaries. Nb21,24) and Ti25,26), which form stable carbides, suppress temper brittleness.

This correlation between temper brittleness and ϵ -carbide does not imply that presence of ϵ -carbide is a sufficient condition for temper brittleness but it does indicate that presence of ϵ -carbide is a necessary condition for temper brittleness.

It may be added that the substructure responds not only to picric acid but also to nitric acid but apparently to no other common etchant[27)].

c. Stress Corrosion of Mild Steel in Nitrate Solutions.

The stress corrosion of mild steel in nitrate solutions indicates some reaction between steel and solution. This reaction should follow the mechanism for the reactions of nitric acid.

The reaction of dissociated HNO_3 on steel according to the formula

$$H\cdot ONO_{2\ ads} \longrightarrow H_{metal} + ONO_{2\ ads}$$

is reversible. Hence, the occurrance of nitrate on a steel surface necessarily leads to formation of nitric acid with the H in the steel, regardless of how this nitrate is formed. When immersed in a nitrate solution, the steel surface thus becomes partly covered by a mixture of absorbed HNO_3 and absorbed H_2O. This mixture is comparatively concentrated in HNO_3 and therefore contains some undissociated HNO_3. The steel surface would become passivated by this undissociated HNO_3 unless the $NO_{2\ ads}$ is reduced to NO_{ads}. This may be effected by the H in ϵ -carbide.

The gaseous products of dilute HNO_3 and C-bearing steel are NH_3, N_2, and the various oxides of N[28, 29)]. This shows the reduction of HNO_3 to atomic N as an intermediate and thereby the possibility of absorption of N by the steel. This reduction of HNO_3 should be accelerated by the presence of an H-rich phase in the steel. There is no formation of NH_3 or N_2 with C-free iron.

There are thus two possible roles of ϵ -carbide in the reaction of steel with a nitrate solution, namely, to destroy passivity and thereby make reaction possible, and to effect reduction of HNO_3 and thereby absorption of N.

The effect of C upon the stress corrosion of mild steel in nitrate solutions has been studied by Parkins[30)]. There was a pronounced effect of the C content upon the time to failure. Whereas cracking occured after a few hours at a C level of 0.07% steel with 0.02% C did not fail in 500 hr. Tempering at and above the 250°C reduced the susceptibility conspicuously, tempering above 300°C reduced it to nil[31]. It follows that some carbide is instrumental in the reaction between the steel and the nitrate solution and that this carbide is ϵ - carbide.

It appears that the ϵ - carbide plays both roles suggested above. First of all, it must destroy passivity, for otherwise no reaction would occur. Second, if it causes absorption of N, the absorbed N may cause brittleness and thereby stress corrosion failure. An embrittling effect of N has been observed in numerous cases, e.g., caustic embrittlement [32, 33], that is another case of stress corrosion, and temper brittleness [25, 34]. Addition of N to high-purity Fe causes intercrystalline brittleness. Fracture in nitrate solutions is intercrystalline[36].

d. Hydrogen-Rich Plase in Titanium.

Huber et al[37] found a phase in heat-treated Ti that was revealed by etching with HNO_3. This phase did not occur in degassed specimens. Radiography by means of added tritium proved that this phase is rich in hydrogen. The conditions for its appearance suggest that it is TiN that, according to Pollard and Woodward[38], contains H.

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