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DEPARTMENT OF METALLURGY
Institute of Metals and Explosives Research

UNIVERSITY OF UTAH
SALT LAKE CITY, UTAH

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A STUDY OF PHYSICAL AND CHEMICAL
PROPERTIES CONTROLLING REPRODUCIBILITY IN
THE INITIATION OF DETONATION
OF LEAD AZIDE

Final Report

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A STUDY OF PHYSICAL AND CHEMICAL PROPERTIES
CONTROLLING REPRODUCIBILITY IN THE INITIATION OF
DETONATION OF LEAD AZIDE

I. Introduction

The following constitutes the Final Report on Sandia Corporation purchase order 13-3126 dealing with the physical and chemical properties controlling reproducibility in the initiation of detonation of lead azide. The investigations carried out may be considered to fall under the following categories:

(1) Electron micrographic investigations of the induction period of lead azide, (2) Decomposition of lead azide in electron bombardment. (As a part of this study techniques were developed for growing films and microcrystals of lead azide sufficiently thin that they could be viewed by transmission in an electron microscope), (3) Photoconductivity of lead azide, (4) The effect of heat treatments and long-term storage treatments upon the sensitivity and chemical composition of colloidal lead azide, (5) The mechanism of lead carbonate formation in lead azide, (6) The effect of certain accelerated treatments upon the sensitivity of lead azide, (7) Crystal growing, and ~~(8) Construction of an Image Converter Camera~~. Technical reports were prepared and submitted to Sandia Corporation during the contract period which described the results under the phases 1, 2, 3, and 5. Hence only brief summaries of these studies will be presented here. The remaining investigations, (exclusive of number 8) which as yet have been only described in the monthly progress letters will be described more completely. Since phase number 8 does not represent a part of the actual lead azide research and since an operation and maintenance manual has been written which describes completely the image converter camera, no further discussion of phase 8 will be included in this report.

As a result of the progress achieved in the study, especially during the present contract period, it is felt that considerable insight has been gained with regard to the important and difficult problem of the factors affecting

reproducibility in the initiation of lead azide. In addition two PhD degrees and two masters degrees have been conferred thus far to graduate students who fulfilled their thesis requirements solely upon research supported by this contract. A paper, "Photoconductivity Electron Micrographs and the Mechanism of Thermal Decomposition of Lead Azide", based largely upon results obtained during the period covered by the previous purchase order 15-6358A was presented during the present contract period at the Tenth Contractors Conference of the Basic Research Group, USA ERDL, Fort Belvoir, Virginia. A second paper based upon results during the present contract period and entitled, "Electron Micrographic and Bombardment Studies of Lead Azide" was presented October 31, 1962 at the Eleventh Contractors Conference of the Basic Research Group.

II. Electron Micrographic Investigation: Induction Period of Alpha-Lead Azide

The results of this study were described in a report of the same title. This report may be summarized briefly as follows: The initial stages of the so called induction period in the thermal decomposition of lead azide is characterized by a high rate of "degassing"; thereafter, the rate of gas evolution drops to a lower and fairly uniform rate. At the end of the induction period the characteristic autocatalytic decomposition commences. It has been shown that the gas evolved during the induction period is mainly hydrogen azide which is one of the products of a hydrolysis reaction between water and α -lead azide, the other product being a form of basic lead azide.

The purpose of the investigation was to observe by electron microscopy the early formation of lead nuclei on α -lead azide and to detect the products of any reactions that might occur on the surface during the induction period. This required the use of crystals and the application of replica techniques. An inherent feature of replication is that in addition to reproducing the contour of the surface, unreactive or insoluble compounds which might have formed on the surface may be caught by the replicating film and extracted from the crystal surface. By this means some of the surface compounds may be lifted from the crystal by the replicating operation and studied in the electron microscope.

The lead azide crystals were decomposed at 250°C for varying times in a special steel furnace at a pressure 0.5 μ Hg. Heat was applied by an electric-

ally powered filament. Normally 10-12 minutes were required for the furnace to attain the 250°C temperature. However, all the decomposition times were measured from the time the filament was turned on. After the desired amount of decomposition the power to the filament was turned off, air was admitted to the apparatus, and the crystals were deposited on a cardboard tray preparatory for replication.

On surfaces of lead azide crystals that were heat-treated, sufficiently tiny lead nuclei were large enough to become visible in the micrographs. This generally occurred at 15 minutes decomposition, these early lead nuclei possessing diameters the order of 0.005 μ and many of them being extracted by the replicating process. Surface films were found to be formed on lead azide crystals during the induction period. These films were evidenced in several ways. Firstly, when such films were extracted by the carbon replica, electron transmission was reduced considerably over the sections of the replica to which the surface film adhered, and thus the presence of the film could be identified. The carbon replica film is very tough and pliable considering how thin it is. When mounting the replica on the grid it may be flexed or bent to quite an extent without suffering much damage. Compared to the carbon film, however, the extracted, secondary films were brittle. Hence, the extracted film suffered a good chance of being broken or cracked with the carbon replica itself remaining intact. This phenomenon afforded, then, a second method for detecting surface film formation on lead azide. When the surface film cracked in this manner, the carbon film could be observed underneath the extracted film, thus affording a good means of identifying the presence of extracted surface film compounds. The surface films in general did not cover the whole crystal. A significant observation of the investigation is that while lead nuclei and surface films were frequently formed in the same vicinity, they were not mixed together. Thus lead speck growth was inhibited by surface film formation. The reason for this result is probably that very small germ lead nuclei react with water before they coalesce into lead nuclei that are large enough to be observed. The reaction between water and germ lead nuclei according to Reitzner⁽¹⁾ is

The water could be present as contamination from an external source absorbed on

the crystal or chemically bound water. Another mechanism for the formation of surface films on lead azide is provided by a hydrolysis reaction between water and lead azide, namely,

which results in a basic lead azide. Reitzner has determined by mass spectrographic analysis that the gas given off during the induction period of thermal decomposition is largely composed of hydrogen azide, ⁽²⁾ and this has been confirmed at this laboratory by chemical tests.

The films observed in this investigation to form during the induction period of thermal decomposition probably resulted from a combination of reactions (1) and (2). The fact that most of the films observed were thin and diffuse may be explained by the small amount of water present. As heating was continued the film formation probably would continue until the water was used up. After the water was gone, the germ nuclei would be free to grow and the normal autocatalytic decomposition,

would occur. As this reaction continues beneath the basic lead azide film that was formed first, apparently, the basic lead azide becomes loosened and is finally released by the crystal, which would explain the observation that where the lead nuclei were visible no basic lead azide film was present. It was possible to replicate an area of the crystal before the basic lead azide film was dislodged by the continuing reaction. Sometimes this film of basic lead azide was trapped and extracted by the carbon film. When the azide was dissolved away by the ceric ammonium nitrate, parts of this basic lead azide film were not dissolved and became the films that were extracted in the carbon replicas and observed in the micrographs.

Carbon replicas of crystals stored in dry atmospheres of oxygen, nitrogen, and air for 26 days at 35°C were also prepared. In these cases also bits of extracted material were observed on the replicas, and the surface topography appeared to be affected considerably. It should be mentioned that insufficient observations were carried out to establish definitely that the features observed were characteristic of the various gaseous environments rather than being features

the untreated crystals, although it was doubtful that the latter was the case because such distinguishing characteristics have not been noted with freshly-grown lead azide crystals.

The effect of treating α -lead azide in carbon dioxide and water vapor was also studied, crystals being exposed for six hours to carbon dioxide at atmospheric pressure saturated with water vapor at temperatures of 70°C and 100°C. This type of treatment produced dense surface films composed of carbonates, the 100°C temperature resulting in extracted films that were so dense in some areas that they were practically opaque to the electron beam.

Crystals of α -lead azide were etched with sodium hydroxide, because this type of treatment was expected to produce a form of basic lead azide on the surface of the crystal. Carbon replicas of such treated crystals proved to extract bits of surface film.

In conclusion, the atmosphere in which lead azide is stored can have a definite effect upon the surface characteristics of the lead azide, and in fact it appears that virtually no atmosphere is completely inert to lead azide. Consequently, the sensitivity may be affected by the atmospheric environment. More concerning this subject will be given later in the report. There seems to be agreement in the literature that water also greatly influences the formation of surface compounds. From this study it has become evident that heating crystals to drive off moisture may lead to the formation of surface compounds which may affect lead speck growth and the sensitivity to initiation.

III. Decomposition of α -lead Azide in Electron Bombardment: The essential results of this investigation were described in a technical report with the above title.

The study included observations in the electron microscope of the decomposition of "standard-azide" crystals and very films and microcrystals of lead azide using the electron beam of an electron microscope to effect the decomposition. The films and microcrystals were sufficiently thin that they could be viewed by electron transmission. As far as is known by the personnel of this laboratory this is the first time anyone has succeeded in growing such thin films and microcrystals of lead azide.

In the initial experiments a small "standard-sized" crystal of good quality was mounted between #200-mesh grids for placement in the electron microscope. The decomposition from electron bombardment was of a different nature than thermal decomposition. Thermal decomposition turned the crystal uniformly to opaque, light yellow, whereas the crystals exposed to electron bombardment changed to a transparent, brown color, and there was a sharp demarcation between areas of the crystal exposed to the electrons and the unexposed areas. It was observed that in electron bombardment cracks rapidly formed, splitting the crystal lengthwise, following which many additional cracks developed, reducing the crystal to smaller and smaller pieces. The final result was a withering and straining of the crystal until it bent at a 90° angle toward the electron source, substantiating the fact that high energy electrons drive-off nitrogen directly from the side of the crystal that is bombarded, collapsing the crystal from that side with a subsequent bending in the direction toward the electron source.

Prior to electron bombardment silhouette views of crystals made with an electron microscope showed the faces to be smooth and free of any nodular growths. This condition changed rapidly during electron bombardment with small spherical shapes or nodules forming and general surface roughening taking place. Since the roughening occurred by virtue of decomposition, it was concluded that some of the small nodules likely were lead specks on the surface. The fact that the growth of these small nodules could be observed as decomposition proceeded served as verification of this conclusion.

A beam of electrons was directed at the tip of a crystal. After fifteen minutes of such bombardment, examination showed the end of the crystal to be brown. With continued bombardment the crystal suddenly broke off close to the point at which it was mounted. Heat was conducted from this smaller crystal segment more rapidly than from the section of the original crystal that was bombarded initially because of the nearness of the metal sample holder. Consequently, a much greater concentration of electrons could be directed on the end without detonation of the crystal. Under an intense electron beam an unusual thing happened; a large bubble began forming at the end of the crystal. The bubble pulsed slightly and increased in size with an increase in electron intensity. Since this whole event occurred within the vacuum of the

electron microscope tube, it was assumed that the gas causing this bubble was nitrogen resulting from the decomposition. It is only conjecture as to the composition of the bubble, although undoubtedly it comprised a surface compound formed during early stages of decomposition. An electron diffraction pattern of the crystal end gave indications of lead being present which would be expected since the crystal had suffered some decomposition.

Thin films of lead azide were grown using an adaptation of a procedure suggested by Joebstl.⁽³⁾ The essential feature of the method was the reaction of HN_3 vapor with a thin lead film that was deposited upon a suitable substrate. To produce such a substrate two drops of 1% collodion solution (dissolved in amyl acetate) were dropped onto the surface of a bowl of distilled water and allowed to dry. Onto this film was placed a number of stainless steel samples grids, stainless steel being used because of its being inert to HN_3 . The grids were then transferred to a microscope slide by placing the microscope slide over the tops of the grids, then quickly moving the slide downward and then upward in a swooping manner. This procedure, when accomplished correctly, resulted in the grids being sandwiched between the collodion film and the microscope slide. The assembly was then dried, placed in a Kinney SC-3 evaporator, and a film of carbon evaporated on the collodion. Following this a very thin layer of lead was evaporated on top of the carbon. A group of grids, after being prepared in the above manner was placed in a sealed bottle with an HN_3 generator and kept in total darkness for 48 to 120 hours. Electron diffraction patterns were made after each stage of the thin film preparation. After 22-120 hrs. reaction time, the pattern consisted of 3 diffuse rings indicating the structure was very amorphous. It was difficult to obtain accurate plane spacings because of the diffuse character of the rings. However, calculations indicated two of the rings were from lead azide (Form 1) structure. The half width of the rings indicated that the crystallites were of an extremely small size on the order of $15 \text{ \AA}$. This was probably due to the way the films of the lead azide formed on the collodion-carbon pair substrate, in all likelihood lying in flat plates.

Under the action of HN_3 vapor much of the original lead film was changed to small islands of lead azide. The mechanism of this movement

isn't entirely understood, i.e., it is not known whether the lead diffused over the surface during the lead azide film formation or whether the lead azide itself diffused during the growth.

Through an alteration of the procedure namely doubling the amount of the HN_3 vapor generating solution and renewing this solution every other day for a 120 hour period to accelerate the reaction as much as possible, numerous very tiny lead azide crystals were grown rather than films. The obvious advantage of these crystals is that because of their extremely small size they could be viewed directly in the electron microscope. Electron diffraction patterns for product analysis could be made of them, and since replica techniques were not required, a continuous visual observation could be maintained on the same crystal during decomposition. Though there are still problems unsolved, the successful production of microcrystals should make possible new studies that promise to contribute additional information about lead azide. For example studies might be made of the rate of growth of lead nuclei in electron and thermal decomposition by measuring the increase of nuclei size during decomposition. Through use of a cold stage it should be possible to isolate fairly well isothermal decomposition and decomposition from electron bombardment. The high resolution of modern electron microscopes makes possible observations of lead nuclei growth almost from their first formation to complete decomposition. By means of thin films or microcrystals it may be possible also to carry out optical absorption measurements for lead azide thereby gaining additional information about the solid state properties of the compound. Such measurements for lead azide have been impossible to perform previously because of the excessive light absorption of standard-sized crystals.

Early stages of crystalline growth were observed by electron micrographs of the microcrystals. The early "seeds" that resulted in lead azide crystals appeared as thin hexagonal plates or as tiny orthorombs. These early stages of growth, however, were transitory and elongation along the [001] direction soon made them similar in appearance to the normal-sized lead azide crystals, though such microcrystals in general were only a few microns long and less than a micron wide.

A number of sequences of electron micrographs showing the decomposition of microcrystals were obtained. Early lead nuclei were visible in these

sequences whose diameters were as small as $80 \text{ \AA}$. By utilizing a cold stage and careful procedures it is expected that the growth of such nuclei may be first observed when the diameter is as small as $30 \text{ \AA}$. The microcrystals upon which these observations were made were so small that they contained only a few lead nuclei, and thus the growth of all of them could be observed simultaneously. Considerable movement of lead was evidenced during the decomposition. Neighboring lead specks coalesced into a single lead clump when they expanded sufficiently to touch each other, the coalescence taking place in a manner similar to the uniting of two drops of water except the process was slower. The end result after complete decomposition was several droplets of lead from each crystal. This process of lead speck growth could be viewed with especially good clarity in the thin hexagonal plates of lead azide where the electron scattering and absorption was less. Cross-section views of decomposed hexagonal plates attested to the fact that lead metal "heaps" up on the surface as decomposition progresses. The migratory behavior of lead with its coalescence into larger droplets may have depended upon the crystal being hot. Possibly the behavior would have been entirely different had a cold stage been used to assure the sample remaining cold during decomposition by electron bombardment.

Electron diffraction techniques were used for interpreting various stages of the substrate preparation, the lead azide film growth, and the decomposition. Both the thin films of lead azide and the microcrystals produced diffuse rings. A spot pattern characteristic of single crystals was not achieved possibly because even the microcrystals were composed of numerous minute crystallites. Larger crystals, instead of diffracting simply "melted away", in which case the diffuse pattern was lost in the background as other rings of differing diameter began forming and sharpening. Possibly a cold stage would be an aid for obtaining diffraction patterns from the larger single microcrystals by reducing thermal decomposition. Analysis of the Debye rings of the initial diffuse diffraction pattern described above showed the diffuse pattern to be the (201) and (303) planes of lead azide. Comparisons between the diffraction pattern of the lead film deposited upon the collodion-carbon substrate and the diffraction pattern which represented a "fingerprint" of lead azide.

decomposed completely by the beam of electrons in a vacuum in the electron microscope revealed a difference. The lead evaporated upon the substrate formed into small islands ($50 \text{ \AA}$ and up in size) which as a consequence probably readily reacts when exposed to the atmosphere. The diffraction pattern of the lead film deposited upon the collodion carbon combination, therefore, likely was influenced by the presence of compounds of lead such as oxides and perhaps carbonates which formed during the interval between removal from the SC-3 evaporator and placement in the electron microscope when the assembly was exposed to the atmosphere.

IV. Photoconductivity of Lead Azide: The results from this study, summarized here, were detailed in a technical report with the above title. Since sufficiently large single crystals could not be grown for the photoconductivity measurements, compressed pellets (generally of $1/8''$ diameter) prepared from small crystals grown at this laboratory or from commercially prepared colloidal lead azide were utilized. The sample holder used to hold the pressed pellets during illumination was constructed of copper and mounted in pyrex dewar flasks to facilitate either cooling or warming the sample as well as evacuating the enclosure to prevent oxidation of the lead azide pellet surface. The pellet was mounted between two spring-loaded silver electrodes electrically insulated from the copper block, electrical connections being made by tungsten leads sealed through the pyrex dewar section. Quartz windows were utilized to permit maximum transmission of light in the ultra violet region. The sample holder was mounted in a plastic block and placed in a Beckman DK-2 spectrophotometer which was used to obtain monochromatic light for radiating the sample. Experiments were also conducted using a Uvis Grating Monochromator supplied by the Farrand Optical Company with a range for $2200 \text{ \AA}$ to $6500 \text{ \AA}$ in place of the Beckman spectrophotometer. The sample was mounted in series with a battery or a d.c. power supply and a Kiethly electrometer with a decade shunt which in combination with the electrometer formed a very sensitive ammeter. Illumination of the lead azide was provided by an Osram HBO-200 high pressure mercury lamp, Model 520-Q supplied by the American Optical Company. Under the influence of the electrical field a small dark current was observed.

This dark current was allowed to reach its maximum value, and then the photocurrent was taken as the increase in current flow resulting from illumination.

The photoconductivity of lead azide was found to be influenced markedly by heat treatments. Runs were made upon batches of colloidal lead azide that were aged for 5, 10, 15, 20, 30, and 40 minutes at 250°C, the samples being heated in an aluminum capsule by plunging it into a molten metal bath at the desired temperature. The photoconductivity measurements were all carried out under the same conditions namely 25°C, 650 mm Hg, and approximately 1575 volts/cm electrical field strength. In the range of 5-40 minutes heat treatment the photoconductivity increased markedly with treatment time with the most rapid increase occurring in the 20-40 minutes interval. The maximum photocurrent occurred in all cases at 4060 Å, and this also was the band that was the most influenced by the heat treatments. Experiments were carried out to determine how the photoconductivity was affected by longer heat-treatment times. In this case the samples were heated in shallow metal trays in a drying oven at 250°C for times ranging from 5 minutes up to 260 minutes. After this treatment the dark current was markedly increased, and it was found impossible to measure photocurrents above the high dark current background. As a function of aging time, the dark current increased very rapidly to a maximum at 15-20 minutes, and thereafter it dropped assuming about a constant value for times greater than 40 minutes. Aging the samples at 250°C in shallow trays in a drying oven apparently had a different effect than did the aging treatments in the metal capsules. This was construed to be the result of less efficient heating in the latter case by virtue of the poor heat conductivity of lead azide and the lower surface area exposed to heating in the metal capsules.

The same pellets used for the above dark current measurements were re-run a second time, with readings being taken after one minute's exposure to the light which was before the current had a chance to reach its maximum. The procedure was then repeated once again to note if any changes occurred as a result of the initial experiments. The general shapes and features of all curves were the same except that the magnitudes of the dark currents were reduced in each succeeding trial. (Interestingly, as will be discussed in the next section, heat treated lead azide was found by the miniature card gap test

and the light ignition test to be the most sensitive for treatment times of 5-20 minutes depending upon the sample of lead azide). On the following day the sample that had been heat-treated for 15 minutes was re-run. Before the dark current had leveled-off the pellet was illuminated at $4060 \text{ \AA}$ to determine the effect of the light. Photoconductivity was observed, and after the illumination was discontinued exponential decay occurred. The dark current, however, continued to increase, and then upon illuminating the sample again the meter pointer began to oscillate, and the sample detonated. Fortunately no serious damage was suffered by the equipment. The sample aged for 20 minutes was mounted in the holder and the field was applied carefully, noting the dark current reading, and when it increased and went off scale on the 10^{-8} ampere range, the potential was quickly removed before explosion occurred. The samples heat-treated 10-20 minutes, for which the dark conductivity was highest, certainly were more sensitive to initiation under illumination and the influence of an electrical field. This probably resulted from an electrical breakdown in the material which occurred more easily after heat treatments of the proper type.

More samples were heat-treated in a similar manner except at 100°C rather than 250°C . In this case the electron donating centers were not emptied by the effect of the electric field alone, and photoconductivity was measured upon illuminating the sample. Curves of dark conductivity and photoconductivity vs treatment time, again with maxima at 10-20 minutes treatment, were obtained. The fact that maxima occurred at about the same treatment times for both 100°C and 250°C was very surprising, and as yet no explanation has been determined for this phenomenon.

Initially the increased photoconductivity and dark conductivity resulting from heat treatments was thought to be due entirely to lead speck formation (colloid centers), the free electrons resulting from ionization of the lead. However, the fact that the conduction curves exhibited maxima at 10-20 minutes while lead speck formation would necessarily continue to increase with decomposition, coupled with the fact that the maximum appeared insensitive to the heat-treatment temperature showed that the situation was more complicated. Active centers other than colloid centers must be produced by heating, and intermediates must occur after 10-15 minutes regardless of the

temperature which tend to annihilate the centers.

The effect of sample thickness was investigated by varying the weight of the samples, holding the diameter constant at $1/8"$, pellets weighing 10, 15, 20, and 25 mg being prepared. The dark current increased with pellet thickness due to the greater number of electron donating centers present, showing that it was a bulk effect. The photocurrent on the other hand decreased with increasing pellet thickness. This decrease was due to the increased number of electron traps, which was a function of volume, and the fact that the irradiated area remained constant since the photoelectrons resulted from the ionization only of those centers located near the illuminated surface of the pellet.

The intensity of the beam emerging from the monochromator was varied in a known manner through the use of neutral density filters, and then the photocurrents were measured at $4060 \text{ \AA}$. The results, when plotted against the square root of intensity fell approximately along a straight line. If it is assumed that the number of photoelectrons equals the number of traps then according to Moss⁽⁴⁾ the photocurrent would be proportional to the intensity.

A very important phase of this investigation was the determination of the photoconductivity of colloidal lead azide samples that had been stored in various dry gaseous atmospheres at 35°C for times up to 80 days. More concerning these treatments will be detailed in the following section. The gases considered were air, argon, carbon dioxide, oxygen, and nitrogen. The photocurrents in the $4060 \text{ \AA}$ band were measured at 26, 65, and 80 day intervals for lead azide stored in each of the above gases except carbon dioxide in which case only the 26 day measurement was performed. For nitrogen, air and oxygen the photoconductivity increased with treatment time, the effect being the most pronounced with nitrogen and the least with oxygen. For example with nitrogen the photoconductivity increased by a factor of nearly 5 as a result of the 80 day treatment. The Argon storage on the other hand brought about a slight drop in photoconductivity. Though only the determination at 26 days was made for the carbon dioxide storage so the results are not conclusive, the effect seemed to be similar to argon. Samples that had been treated in nitrogen for 65 and 80 days, then stored in the dark in a hard rubber container at room temperature for 4 weeks, were run at $4060 \text{ \AA}$. The photoconductivity in both

cases was found to be 20-25% less than when the measurements were made immediately after removal from storage, indicating a drop in the number of electron donating centers. In order to determine if the number of these centers could be greatly reduced or eliminated entirely, new samples were run after having been treated for 65 days and 80 days in the nitrogen atmosphere and then being placed in a vacuum oven at 100°C for 4 hours and for 16 hours. The 16 hours evacuation reduced the photoconductivity the greater amount. However in both cases the photocurrents were much lower than those obtained from the non-aged control samples. (The effect upon sensitivity of the long-term storage will be described in the next section).

The increased photoconductivity from extended storage in nitrogen and to a lesser extent storage in oxygen must have been the result of an increased concentration of active centers in the crystals rather than simply an adsorption of gas on the surfaces. Firstly, gas adsorption would not be expected to exert such a large effect. Secondly, significant increases in photoconductivity were noted for the entire 80 day period, and adsorption would not be expected to continue for this length of time. The centers introduced into the crystal are believed to be due to the incorporation of atoms (primarily nitrogen) into the lattice in intersititial positions. Nitrogen molecules apparently adsorb on the lead azide and dissociate into atoms which eventually find their way into interstitial positions in the lattice. The presence of these intersititial nitrogen atoms (V_1 centers) leads to the formation of centers which promote the photoconductivity of lead azide. One way in which the V_1 centers might contribute an electron is as follows:

The nitrogen atoms could dissociate and enter the lattice as atoms reforming the V_1 centers or diffuse to the surface and escape. The latter could account for the diffusion constant reported by Dodd⁽⁵⁾ and would be the rate controlling step. The presence of the N_4^- radical has been confirmed by Shuskus,

et. al.⁽⁶⁾ in potassium azide where it was reported to be a linear configuration stable only at low temperatures. This configuration has also been discussed by King, et. al.⁽⁷⁾ in sodium azide. Nitrogen atoms are known to be present, especially at higher temperatures, as products of thermolysis by the mass spectrographic work of Dodd.⁽⁸⁾

From the spectral distribution of the photocurrent the following absorption bands were identified: 3650, 4060, 4350, 5400, and 5800 Å. It should be stated that some of these bands were quite indistinct. However, results were sufficiently reproducible that they all appeared to be real. Suggestions as to the possible origin of each of these bands were advanced as follows.

A. 3650 Å

This band was believed to be due to the ionization of excitons. The excitons are believed to be formed by the photolytic decomposition of the lead azide molecule which may be represented as follows:

This results in the formation of a positive hole and a conduction electron.

B. 4060 Å

This was by far the most prominent band in the photoconduction of lead azide. It is believed to be due in part to V_1 centers as explained previously and possibly also to colloid centers. That the photocurrents obtained from the ionization of colloid centers at this wavelength were much less than for other centers involved was evidenced by the low photoconductivity measured for lead azide which had been evacuated for 4 hours and 16 hours. The 4060 Å band incidently is just beyond the absorption edge which occurs at 4000 Å. Photolysis should occur at the absorption edge and at shorter wavelengths within the absorption band since the energy is essentially all absorbed and is of sufficient intensity to cause photolytic decomposition, but it should not occur for wavelengths longer than 4000 Å.

C. 4300 Å

As yet the origin of this band is unknown. It appeared only in a sample aged at 250°C for 15 minutes. It possibly has an important bearing on sensitivity as it was a pellet pressed from this sample that detonated in the sample holder under influence of the electric field shortly after illumination was commenced.

D. 5400 Å

This band is approximately the same size as the F band and might in some manner be associated with it. One possibility could be a β -band caused by an excited electron on an anion near an F center. Another possibility could be an R_1 -center (two neighboring anion valencies with an associated electron). Both of these centers could contribute an electron to the conduction band.

E. 5800 Å

This band is believed to be due to F centers. This is the region where F centers are usually located, and they were definitely present since the samples became colored as a result of illumination.

V. The Effect of Heat Treatments and Long-term Storage Treatments on the Sensitivity and the Chemical Composition of Colloidal Lead Azide

Introduction

Some precision explosive devices in which lead azide is used require lead azide whose sensitivity is highly reproducible. Though there are some factors such as particle size and gross impurities, for example, which are known to affect the sensitivity of lead azide, apparently there are other much more subtle factors which are unknown and exert sufficient influence on the sensitivity to render some batches of lead azide unusable in precision explosive devices. The purpose of this investigation was to identify some of these subtle factors and to determine how they might come into importance. The procedure followed was to expose a "standard" colloidal lead azide to various controlled treatments and then to compare the resulting sensitivities with a control sample. In addition to the sensitivity tests lead azide value determinations, i.e., determinations of the percentage of the sample that was lead azide, were made by the cerate oxidimetry method.

The controlled treatments consisted of (1) partial thermal decomposition of lead azide at 250°C and (2) long term storage in the absence of light at approximately ambient temperature conditions in atmospheres of pure oxygen, nitrogen, argon, and air. Results of treatments in carbon dioxide and water vapor are described in Section VI and will be mentioned also in Section VII with regard to influences upon sensitivity.

The partial thermal decomposition treatments were selected because of the "memory effect" exhibited by lead azide in the thermal explosion test.⁽⁹⁾ In this test, which consists of measuring the induction time to explosion when an explosive is abruptly heated to a temperature equal to or above the explosion temperature, lead azide exhibited the property of possessing a fixed total induction time for a given temperature irrespective of whether the heating was carried out in increments or in one step. In addition, electron micrographs of lead azide crystal surfaces after various stages of decomposition, which have been obtained at the Institute of Metals and Explosives Research, showed the growth of the specks on lead azide crystal surfaces during decomposition.⁽¹⁰⁾ As a result of that investigation a mechanism for the thermal decomposition of lead azide was proposed, according to which the growth of lead specks catalyzed the decomposition.

The long term atmospheric aging treatments were selected because early tests of sensitivity carried out on a sample that had been dried and stored indicated a change in sensitivity with time. To determine if the sensitivity changes were real and also to ascertain the causes, long term controlled storage treatments were carried out in the various separate gases comprising the earth's atmosphere. Argon, which was considered to be inert was used as a control.

The sensitivity tests to be applied to the control samples and the treated samples were required to be reproducible, capable of differentiating small differences in sensitivity, and in addition it was essential that the tests only require small quantities of explosives for making a determination of sensitivity.

There are a variety of methods for measuring relative sensitivity that have been devised for predicting the initiation behavior of primary explosives. These include sensitivity to impact, to shock, to friction, to spark,

and other types of electrical discharge, sensitivity to pinching of the explosives between metal surfaces, propagation sensitivity at and near the critical diameter, measurements of the minimum primer or booster required to obtain a detonation capable of propagation, and determinations of the amount of an inert substance that may be incorporated in the explosive charge before it becomes too insensitive to detonate or at least to sustain a detonation wave in a suitably long column. Many of such tests have been described in the literature, and have been designated as follows: (1) drop test, (2) thermal ignition test, (3) friction test, (4) grit sensitivity of explosives, (5) sensitivity of explosives to initiation by electrostatic discharges, (6) the air-gap sensitivity test, and (7) modified card-gap sensitivity test.

The "light ignition" test was selected as one of the tests to be used to investigate the sensitivity of the colloidal lead azide under the varying conditions of this study because this test has proven to be both sensitive and reproducible.⁽¹¹⁾ Using a series of about 20-30 trials, it was found generally possible to establish a 95% confidence interval whose length was only 3-4% of the 50/50 point expressed in terms of the voltage of the capacitor bank that discharged across a gap to produce the light effecting the detonation. This degree of precision was usually sufficient to detect definite differences in various samples of lead azide. There are other advantages possessed by this test, namely (1) only a small quantity of explosive is required for a sensitivity determination, and (2) the test can be carried out with relative ease and rapidity. Sensitivity was also evaluated by a "hot wire" test which was developed for use in this study. This test was conceived to duplicate approximately the conditions of initiation under which lead azide is most commonly used in explosive devices. The third standard test used in this study was the determination of the lead azide content of the sample. This assay was carried out by the cerate oximetry method. Two determinations were made in each case for use in comparing the treated and the standard samples.

Experimental Method and Apparatus

A. Light Ignition Test for the Sensitivity of Colloidal Lead Azide

The so-called "light ignition" test where the explosive is initiated by light from the discharge of a capacitor bank across a gap between two electrodes was devised by Eggert, et. al. (12). In the present investigation, tests were usually made on a conical shaped explosive sample loaded from a conical shaped spoon on a copper plate. By taking careful precautions good reproducibility was obtained in the test. The sensitivity was represented by the expression $V_i - V_f$ where V_i was the initial capacitor voltage and V_f was the residual after discharge. The potential of the charged capacitors was measured by a high voltage voltmeter before discharge between two electrodes. The residual voltage of the capacitor bank was measured by a low voltage voltmeter. An advantage of this test lies in the speed with which high energies can be applied to explosives and the ease with which the incident energy can be monitored.

The capacitor bank consisted of three 4000 volt 125 ufd capacitors mounted in parallel. They were charged by a 4000 volt power supply to the particular potential desired for the test and then discharged through a 2 mm gap between two steel electrodes which were 1/4" in diameter and 6" long with a 60° taper on the ends. This gap was set carefully to the 2 mm value before each trial because considerable metal was removed from the electrodes during the discharge. After the capacitor bank was charged to the proper voltage, but prior to the discharge, the potential of the capacitor bank appeared across the gap, the electric field strength not being sufficient to produce breakdown. Electrical breakdown and subsequent discharge was effected, however, by a third electrode placed in the gap which upon closure of a foot-switch was charged to 30 KV by another power supply, corona from this charged electrode producing ionization which preceded the breakdown. It is important to note that a reproducible light flash could be obtained if, and only if, the trigger electrode were discharged to the earthed steel electrode.

The initial voltage across the capacitor bank was measured with a 5 KV voltmeter. The residual voltage after the discharge was also measured using a 300 V voltmeter. The energy expended in the arc was considered to be proportional to the difference between the initial and residual voltages. Fig. 1 is a schematic diagram of the system.

- A. Power supply, max = 4000V
- B. Power supply, 30,000V, 15 MA
- C. Steel electrode
- D. Trigger electrode
- E. High voltage voltmeter
- F. Morse Key
- G. Low voltage voltmeter

Fig. 1: Electrical schematic diagram of the light ignition system.

With the three 125 ufd capacitors charged to their full rated 4000 volt capacity it was not found possible to initiate the least sensitive samples of lead azide when the azide was at ambient temperature. Consequently, the tests were carried out at elevated temperatures. In order to accomplish this, a hot-plate connected to a temperature controller was mounted immediately underneath the two electrodes. The top of the hot plate was a copper plate that was spaced precisely 0.3" below the electrodes and upon which the lead azide sample to be tested was placed. A glass microslide was inserted between the spark gap and the lead azide which served to reduce the shock generated by the spark (see Fig. 2 for a diagram of the physical layout). Besides maintaining the spacing precisely constant between the electrodes and the test sample it was also found essential to maintain the temperature of the hot plate constant. The light ignition test, in fact, proved so sensitive to temperature variation that during initial experiments with some lead azide which could be initiated at room temperature, variation in ambient temperature such as exists between mornings and afternoons could be easily detected. The temperature chosen for the tests was 150°C. This was sufficiently high that the least sensitive samples could be initiated with the system, but it was not considered high enough that significant decomposition occurred during the short space of time (20 seconds or so) that the lead azide remained on the hot stage before the capacitors were discharged across the gap.

In each trial 35 mg of powdered colloidal lead azide were placed on the copper plate below the spark gap with a lucite spoon which was specially made in conical shape. Tests were carried out using the "up and down" method developed by Dixon and Mood⁽¹³⁾ for the drop test. In general, 24 trials were carried out in each sequence to evaluate the 50/50 point of a sample, the voltage increment between trials being 25 V. Statistical analyses of the results were then carried out to determine the confidence interval for the 50/50 point at the 95% level.

Some improvements over the original application of the light ignition test at this laboratory were as follows: (1) a little coil furnace was replaced with a hot plate capable of attaining about 600°F; (2) the unit was rebuilt to accommodate closer control of the arc distance and electrode

- A. Trigger electrodes
- B. Steel electrodes 6" long, 1/4" diameter
- C. Spark gap, 2 mm
- D. Micro-slide
- E. Colloidal Lead azide (powder)
- F. Copper plate
- G. Thermocouple
- H. Hot Plate
- I. Temperature setting knob
- J. To temperature controller and indicator

Fig. 2: Physical layout of the light ignition apparatus.

alignment with greater ease of electrode removal for reconditioning; (3) arcing the electrodes with the voltage roughly around 50/50 point before use was found to add to the reproducibility; (4) the electrode ends were shaped on a lathe at the constant angle of 60° which led to improved reproducibility, and (5) the push button firing switch was replaced by a foot-switch allowing more convenient operation.

B. Hot Wire Test for the Sensitivity of Colloidal Lead Azide

The hot wire test was devised for the purpose of determining sensitivity under conditions approximating those encountered in the widely used hot wire method of initiating primary explosives. In general, the problem frequently encountered, especially when one is searching for small differences in the behavior of two explosives, is lack of reproducibility of a sensitivity test. Unfortunately, the hot wire test was also found to suffer in this regard. A modification of the original hot wire holding device led to improvement, however. This test utilized a small wire held between two supports and passing through a small sample of the primary explosive under study. It was difficult to measure the temperature of the wire due to heat loss by radiation and conduction, but provision was made to measure voltage, current, and the time lag to initiation.

The electrical energy input into the wire and its temperature are directly related if the time lag to initiation is sufficiently short that the process can be treated as being approximately adiabatic. It was not felt that this could be justified, however, as the transfer of the heat to the explosive was necessary to give detonation.

Selection of a suitable wire and wire size was based on calculations as follows:

$$dH = (V^2/R)dt \quad (6)$$

in which H is the heat resulting from the current produced by a constant voltage V when flowing through a wire of resistance R under adiabatic conditions. The temperature produced depends upon the heat capacity of the wire so that one may write

$$dH = Cd\theta, \quad (7)$$

where C is the specific heat of the wire and θ is the temperature. Fairly good data on the resistance and specific heat of various metals as functions of the temperature are available to be used in equation (8), which was derived by combining equations (6) and (7) to calculate the temperature of a wire as a function of time.

$$(V^2/R) dT = Cd\theta \quad (8)$$

The electromotive force was generated by a set of dry cells wired in series-parallel arrangement so as to provide three volts open circuit voltage. Fig. 3 is a schematic diagram of hot wire test, and Fig. 4 shows the hot wire explosion unit.

The experimental procedure was as follows: The resistance of the 0-10 sliding resistor, which was divided into 32 intervals, was set equal to the resistance of the hot wire. This allowed for adjustment to the desired current flow through the hot wire, using instead of the hot wire, the variable resistor. The current adjustments were made by means of the 0-50 resistance unit which consisted of 2 resistors (10 and 40). The wire was then mounted between the electrodes taking care that there were no kinks in the wire. Thirty-five mg of colloidal lead azide were placed on the copper plate below the electrodes surrounding the hot wire using a conical shaped lucite spoon. The distance between the wire and plate was 1.5 mm, which located the wire in about the middle of the height of the sample. The toggle switch disconnected the variable resistance which was in parallel with the electrodes. The voltage across the hot wire element, and the current through it were measured simultaneously with a voltmeter and an ammeter, allowing calculation of the power delivered to the hot wire. The delay time between the instant the current was turned on and the instant that the explosion occurred was measured automatically to within 0.1 sec by an electric timer. The timer was started by the closure of a double pole, double throw switch which also connected the batteries to the hot wire element. The timer was stopped at the instant of explosion by an acoustical pickup and appropriate electronic circuitry. After a detonation the voltage was decreased an increment for the next trial following the "up and down" method of testing. The 50/50 go-no go point and the 95% confidence interval were determined

Fig. 5: Schematic diagram of hot wire test.

- A. Electrodes
- B. Sample (colloidal PbN₆)
- C. Wire (nichrome or manganin)
- D. Copper plate

Fig. 4: Hot wire explosion unit.

using procedures identical with those used for the light ignition test. (11)

Due to the more erratic nature of the "hot wire" test there were not sufficient amounts of the treated materials available for establishing an accurate 50/50 point, more than half the original samples having to be used to locate roughly the 50/50 point. This left too little material for making accurate determinations. While more samples could have been aged, the new samples likely would have had different properties and comparisons would have been useless.

Nichrome wire was used originally for the hot wire. Its resistance increased slightly as a result of the temperature rise occurring during the induction time to explosion. This change, however, proved to be so small that it was barely perceptible on the meters that were being used. More important considerations were oxidation of the nichrome wire and the ambient temperature. Differences in results between mornings and afternoons were noted as a result of changes in the ambient temperature. Formation of an oxide coating on the surface of the nichrome wire reduced the heat conductivity and consequently the rate of heat transfer to the explosive. The latter was the main reason why the desired voltage was set up using the 0-1 Ω variable resistance which matched the resistance of the hot wire. This expedient minimized the formation of the oxide coating on the hot wire, the wire in this case carrying current only during the time lag to initiation because the desired adjustment on high precision 0-5 Ω resistance was made without current flowing through the nichrome wire.

Later on manganin wires were used instead of the nichrome wire. The characteristics of this wire were more suitable than nichrome so the results were a little more reproducible than with the Cr-Ni wire, but they were still not as good as desired. The main reason for the difficulty was attributed to the resistance of the wire per unit length not being sufficiently reproducible.

C. Statistical Analyses of the Results

The "go-no go" test results were analyzed to determine the 50/50 point and its confidence interval at the 95% level as illustrated by the following example for a non-treated sample of colloidal lead azide evaluated in the

light ignition test. Table A is a summary of the "up and down" test results given in Fig. A.

Table A

V_i	N	Y	%Y	%N Above 50-50	%Y Below 50-50
2400	0	2	100.0	0.0	--
2375	2	2	50.0	50.0	--
2350	2	3	60.0	40.0	60.0
2325	3	0	0.0	100.0	0.0

Table B

V_i	ΣN	ΣY	% ΣN	% ΣY	$V_i - \bar{V}^*$
2400	0	7	0.0	100.0	43.8
2375	2	5	28.6	71.4	18.8
2350	4	3	57.1	42.9	6.2
2325	7	0	100.0	0.0	31.2

Tables A and B are based on the results from Fig. A.

*Note: The sign ($V_i - \bar{V}$) is omitted.

$$\bar{V} = 2375 - \frac{71.4 - 50.0}{71.4 - 42.9} \times 25 = 2356.2 \text{ volts}$$

(The symbols N and Y correspond to a "no" and a "yes" detonation, respectively.) For purposes of determining the 50/50 point the following procedure was adopted. If a trial yielded a "yes" detonation, say at $V_i = 2375$, it was assumed that under the same conditions for that particular trial there would also have been an initiation for any $V_i > 2375$. Likewise, if a trial at 2375 volts registered a failure, it was assumed that failures would have occurred for any $V_i < 2375$. Applying these principles to actual trials, the results shown in Table B were obtained.

Either from the % N or % Y column it is evident that the 50/50 point is between 2350 and 2375 volts. The exact point is calculated by linear extrapolation using either one of the columns. Using the % ΣY column the 50/50

Fig. A: Go-no go results in the light ignition test for colloidal lead azide (non-aged).

point is given by the value of $\bar{V}$. The same result would be obtained if the $\% \Sigma N$ column is used.

D. Estimation of the Confidence Interval

Assume:

(1) the whole test series represents one sample whose mean is defined as the 50/50 point, and

(2) that the percentage Y's below the 50/50 point and percentage N's above the 50/50 point are normally distributed. Thus, if this is true the sample means are normally distributed about the true population mean. (14)
Under assumptions (1) and (2) the quantity

$$t = \frac{\bar{V} - u}{\left[\frac{\sum (V_i - \bar{V})^2}{n(n-1)} \right]^{1/2}}$$

has the "t" distribution with (n-1) degrees of freedom where u is the true sample mean or the true 50/50 point. $\bar{V}$ is the 50/50 point determined from a test series and n is the sample size. Using the data of Table B

$$\begin{aligned} \sum (V_i - \bar{V})^2 &= 0 \times 43.8^2 + 2 \times 18.8^2 + 3 \times 6.2^2 + 0 \times 31.2^2 \\ &= 0 + 705 + 115.2 + 0 \\ &= 820.2 \end{aligned}$$

$$\therefore t = \frac{2584.9 - u}{\left[\frac{820.2}{n(n-1)} \right]^{1/2}}$$

If the sample size is taken as $n = 0 + 2 + 3 + 0 = 5$, then

$$t = \frac{2584.9 - u}{\left[\frac{820.2}{5 \times 4} \right]^{1/2}} = \frac{2584.9 - u}{6.4}$$

For 95% confidence limit we should have

$$p(-t_{0.05} < t < t_{0.05}) = \int_{-t_{0.05}}^{t_{0.05}} f(t, n-1) dt = 0.95$$

If the limits $-t_{0.05}$ and $t_{0.05}$ are computed one can determine u as follows:

$$p(-t_{0.05} < t < t_{0.05}) = 0.95$$

Substituting for t one obtains,

$$p(-t_{0.05} < \frac{\bar{V} - u}{\sqrt{\frac{\sum(V_i - \bar{V})^2}{n(n-1)}}} < t_{0.05}) = 0.95 \quad (9)$$

This involves only the unknown parameter u if $t_{0.05}$ is known. The number $t_{0.05}$ is called the 5% level of t and locates points which cut off 2.5% of area under $f(t)$ on each tail of the distribution. Since $f(t)$ is symmetric about $t = 0$, equation (1) gives the minimum 95% confidence interval, $t_{0.05}$ being determined from standard tables for the cumulative t distribution function. Thus, for the given sample under the column 0.975 for $n = 5$ (or 4 degrees of freedom) one finds $t_{0.05} = 2.78$. Therefore,

$$-2.78 < \frac{2356.2 - u}{6.4} < 2.78$$

or

$$-17.8 < 2356.2 - u < 17.8$$

$$\therefore u = 2356.2 \pm 17.8 \text{ volts}$$

E. Chemical Analysis of Lead Azide by Cerate Oxidimetry ⁽¹⁵⁾

1. Principles

Lead azide is a salt of hydrazoic acid, HN_3 (azimode). Various methods for determining the azide value of lead azide have been proposed and used. A widely used procedure is by determination of the nitrogen content based on the reaction of ammonium hexanitratocerate and lead azide according to the following equation:

In carrying out the procedure excess ammonium hexanitratocerate is added, and the excess is titrated with ferrous sulfate employing O-phenanthroline ferrous complex as the indicator.

2. Reagents

(a) Ammonium hexanitratocerate, $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, molecular weight 548.25, 0.1N in 1N nitric acid. Dissolve 54.8 grams of ammonium hexanitratocerate in 60 cc of concentrated nitric acid (70% specific gravity 1.42) and 40 cc of water. Stir well. Add 4 cc of nitric acid plus 96 cc of water and stir well. Dilute slowly to 1 liter with water, stirring continuously. Protect solution from light. ⁽¹⁶⁾

(b) O-Phenanthroline ferrous complex, indicator solution. To 1000 ml of ferrous sulfate, 0.925 molar solution, add 14.85 grams of O-phenanthroline monohydrate, $\text{C}_{12}\text{H}_8\text{N}_2\text{H}_2\text{O}$. ⁽¹⁷⁾

(c) Sodium oxalate (primary standard grade), supply dried at 100°C for two hours

3. Standardization of Ammonium Hexanitratocerate Solution

Direct method with sodium oxalate ⁽¹⁶⁾ - weigh accurately 0.3000 gram of primary grade sodium oxalate, previously dried for two hours at 100°C and place in a 250 ml Erlenmeyer flask. Moisten with 10 ml of distilled water, add 75 ml of 1.0 molar sulfuric acid, and run in 50 ml of ammonium hexanitratocerate from a buret. Heat to 50° and allow to cool to room temperature. Add one drop of the indicator and titrate the excess ammonium hexanitratocerate with approximately 0.1N ferrous sulfate solution prepared as above.

Titrate 50 ml of the cerate solution with the ferrous sulfate solution, following the above procedure.

Calculation: Where a = ml ferrous sulfate required to reduce 50 ml of cerate solution

b = ml ferrous sulfate solution required to reduce excess cerate solution

w = weight of sodium oxalate

Equivalent weight of $\text{Na}_2\text{C}_2\text{O}_4 = 67.01$.

$$\text{Cerate normality} = \frac{w \times 1000}{67.01 \times (50 - \frac{50b}{a})} \quad (11)$$

4. Procedure for Azide Value Determination for Lead Azide

Accurately weight 0.3000 gram of lead azide on a small paper scoop and place in a 250 ml Erlenmeyer flask containing a small amount of water on the bottom to cushion the fall of the azide powder or crystals. Add to the flask 50 ml of distilled water and 50 ml of standard 0.1N ammonium hexanitratocerate solution from a calibrated buret. Gently agitate the flask during the addition of the cerate and wash down the sides of the flask with a small amount of distilled water at the completion of this operation. After addition of one drop of indicator, titrate the excess cerate with ferrous sulfate solution (prepared as above); the end point is a sharp change from pale green to reddish yellow. At the end point the solution should be as closely as practical to 1 molar of sulfuric acid concentration. If it is necessary to add extra sulfuric acid for this adjustment, the previously calculated acid should be added close to the end point. A blank determination is also run. Once the titration is commenced, it should be completed as speedily as possible because of the presence of plumbous ions in the solution.

Calculation; Since the cerate solution is more stable than the ferrous sulfate, it should be considered as the standard solution in the procedure. However, it must be standardized periodically. For ease of calculation, the normality of the ferrous sulfate is computed daily from the blank runs using the existing normality of the cerate.

Where a = ml of ferrous sulfate to reduce 50 ml of cerate solution of known normality.

b = ml of ferrous sulfate to reduce excess cerate solution

X = normality of the ferrous sulfate, computed daily from readings obtained at

w = weight of lead azide taken.

Equivalent weight of lead azide - $1/2\text{Pb}(\text{N}_3)_2 = 145.63$.

$$\text{Lead azide value} = \frac{(a-b) \times X \times 14.563}{w} \quad (12)$$

The results of lead azide value for the different samples, either commercial lead azide or the samples that were treated in our laboratory, were based on the calculation from equations (11) and (12).

F. Aging Unit Designs

1. Partial Decomposition Heat Treatment of Colloidal Lead Azide

A special furnace was built and placed in a metal box that possessed sufficient strength and was tight enough to eliminate hazard to the operator should an explosion occur inside. The furnace was designed to hold enough lead-tin alloy to allow immersion of a 1/4" diameter 2" length copper cap containing 500 mg. of colloidal lead azide that was to be treated. After melting the alloy and adjusting the power with a variac to maintain a constant temperature, as determined with a thermocouple, the copper cap and its contents were fastened to a 1/4" diameter rod which extended down through the roof of the box. After closing the box door nearly shut the cap was inserted into the molten alloy by lowering the 1/4" rod to the proper distance. When the desired time of treatment was completed the rod was raised to lift the azide out of the furnace, where it was allowed to cool before handling. The process was repeated if necessary to obtain the required amount of azide for experimental purposes. All treated batches were mixed thoroughly before using.

2. Long-term Treatments of Colloidal Lead Azide Stored in Different Gases

Long-term storage treatments of colloidal lead azide under complete darkness at 35°C in O₂, N₂, air and argon atmospheres were carried out. An assembly for achieving these controlled storage treatments was constructed and installed in a compartmental plywood box. The gases were passed over colloidal azide for the desired lengths of time, and then samples were removed to be tested. The design and construction of the aging unit was briefly as follows: It consisted of a box made of 1" plywood with the top cover hinged to open for placement or removal of the samples. The inside dimensions were approximately 20" x 20" x 17". A large resistance plate was placed in the bottom which acted as a heating element, power at about 35 volts being taken from a variac by the heating element. The temperature was controlled with a mercury contact regulator capable of controlling to about 0.01°C. A thermometer was also placed in the box to indicate temperature deviations. To assure greater safety, a piece of styrofoam was placed between the plate resistor heater and the 36 steel plate compartments which

separated the lead azide samples being treated. Its dimensions were approximately 19-1/2" x 19-1/2" x 2". At the center of each compartment a hole 1" in diameter and 1-1/2" in depth was drilled into the styrofoam to house test tubes, each of which contained three grams of lead azide. The test tubes were wrapped with several layers of black electrical tape to keep light out and to reduce flying glass in case of an explosion. The compartment depth was about 6", and each compartment was about 3" square. Six of the above 1" diameter test tubes lying in a row were connected in series through glass leads and rubber hoses fitting into two hole stoppers. The gas entered and left each test tube at a position somewhat below the rubber stoppers reaching the sample at the bottom of each test tube by movement and diffusion. The lines and test tubes in those groups which were treated in the dark were covered with black electrical tape. The flow of gases used (oxygen, nitrogen, air, and argon) were controlled with needle valves, the rate of flow being gauged by the rate the gas bubbled through vacuum pump oil in a U tube at the entering side of the treatment box. A second U tube was filled with cotton to collect any dirt or oil spray which might otherwise reach the samples. A third U tube on the exit end of the series confirmed the exit flow of gas and the tightness of the systems. When a run was finished the test tube stopper was taken off and the test tube removed. The test tube that was removed was replaced with an empty tube to keep the gas moving. An air stirring mechanism powered by a small jet of air from an air compressor was mounted in the treatment box to maintain the temperature as uniform as possible.

Rapid drying of colloidal azide in complete darkness for use in the long range storage tests was performed in a "blackened" desiccator. A blower fastened on the wall outside the primary explosive laboratory supplied air through a 3/4" hose to a large hole through a rubber stopper in the desiccator lid. Eight small holes around the large hole allowed the air and moisture from the lead azide to escape.

III. Experimental Results

A. Results from Partial Decomposition Heat Treatments

The results in the light ignition test for the colloidal lead azide samples treated at 250°C for the various amounts of time, 0, 5, 10, 12.5,

15, 17.5, 20 and 30 minutes are given in Tables I-VIII together with the 50/50 points and the corresponding 95% confidence intervals, while Table IX is a summary of the results from Tables I-VIII. The columns in these tables assume the same meaning as those of Tables A and B. The results in the hot wire test for the colloidal lead azide samples treated at 250°C for the varying times 0, 5, 10, 15, 20, and 30 minutes are presented in Tables X-XV, and Table XVI is a summary of Tables X-XV.

B. Results from Long-Term Treatments

The results in the light ignition tests for colloidal lead azide after long-term storage treatments under complete darkness at 35°C in O_2 , N_2 , air, and argon for the various lengths of time, 26, 65, and 80 days, compared with standard PbN_6 (non-aged) are presented in Tables XVII-XXIX, and Table XXX is a summary of Tables XVII-XXIX.

Table XXXI gives the lead azide content of each colloidal lead azide sample after long-term treatments under complete darkness at 35°C in O_2 , N_2 , air and argon after 26, 65, and 80 days, together with comparisons with standard colloidal lead azide. In this table are also given the lead azide content for some commercial samples. The deviations were 0-0.6% which were quite small compared with the lead azide content. The above determinations could be quite accurate because the $(NH_4)_2Ce(NO_3)_6$ solution was carefully standardized each time before the chemical analyses for azide content by cerate oxidimetry method were carried out.

Discussion

A. Heat Treatment or Partial Decomposition of Lead Azide

Upon comparison of results in Table IX and Table XVI one will note that the sensitivities in hot wire test as a function of the length of heat treatment corresponded fairly well except for the important fact that the light ignition test revealed an increased sensitivity with respect to the standard sample as a result of 5 minutes and 10 minutes heat treatment. Further heat treatments reduced the sensitivity to ignition by light. The sensitivity in the hot wire test, on the other hand, showed no such maximum for intermediate aging times but continued to decrease

Table I: Statistical analysis of data obtained in light ignition test with colloidal PbN₆ (non-aged) with computed 50/50 voltage and 95% confidence interval.

V_i	N	Y	ΣN	ΣY	% ΣN	% ΣY	$V_i - \bar{V}$
2400	0	2	0	7	0.0	100.0	43.8
2375	2	2	2	5	28.6	71.4	18.8
2350	2	3	4	3	57.1	42.9	6.2
2325	3	0	7	0	100.0	0.0	31.2

$\bar{V} = 2356.2$ volts

$n = 5$

$$\left[\frac{\Sigma (V_i - \bar{V})^2}{n(n-1)} \right]^{1/2} = 6.4$$

$u = 2356.2 \pm 17.8$ volts for 4 degrees of freedom

Table II: Statistical analysis of data obtained in light ignition test with colloidal PbN₆ aged 5 minutes at 250°C with computed 50/50 voltage and 95% confidence interval.

V_i	N	Y	ΣN	ΣY	% ΣN	% ΣY	$V_i - \bar{V}$
2225	1	1	1	3	25.0	75.0	17.85
2200	2	1	3	2	60.0	40.0	7.15
2175	2	1	5	1	83.3	16.7	32.15
2150	2	0	7	0	100.0	0.0	57.15

$\bar{V} = 2207.15$ volts

$n = 4$

$$\left[\frac{\Sigma (V_i - \bar{V})^2}{n(n-1)} \right]^{1/2} = 10.93$$

$u = 2207.15 \pm 34.8$ volts for 3 degrees of freedom

Table III: Statistical analysis of data obtained in light ignition test with colloidal PbN₆ aged 10 minutes at 250°C with computed 50/50 voltage and 95% confidence interval.

V_i	N	Y	ΣN	ΣY	% ΣN	% ΣY	$V_i - \bar{V}$
2375	0	2	0	8	0.0	100.0	54.5
2350	2	2	2	6	25.0	75.0	29.4
2325	1	3	3	4	42.9	57.1	4.4
2300	2	1	5	1	83.3	16.7	20.6
2275	1	0	6	0	100.0	0.0	45.6

$\bar{V} = 2320.6$ volts

$n = 6$

$$\left[\frac{\Sigma(V_i - \bar{V})^2}{n(n-1)} \right]^{1/2} = 8.58$$

$u = 2320.6 \pm 22$ volts for 5 degrees of freedom

Table IV: Statistical analysis of data obtained in light ignition test with colloidal PbN₆ aged 12.5 minutes at 250°C with computed 50/50 voltage and 95% confidence interval.

V_i	N	Y	ΣN	ΣY	% ΣN	% ΣY	$V_i - \bar{V}$
2450	0	1	0	6	0.0	100.0	41.7
2425	1	3	1	5	16.7	83.3	16.7
2400	3	3	4	2	66.7	33.3	8.3
2375	2	0	6	0	100.0	0.0	33.3

$\bar{V} = 2408.3$ volts

$n = 3$

$$\left[\frac{\Sigma(V_i - \bar{V})^2}{n(n-1)} \right]^{1/2} = 8.26$$

$u = 2408.3 \pm 35.6$ volts for 2 degrees of freedom

Table V: Statistical analysis of data obtained in light ignition test with colloidal PbN₆ aged 15 minutes at 250°C with computed 50/50 voltage and 95% confidence level.

V_i	N	Y	ΣN	ΣY	% ΣN	% ΣY	$V_i - \bar{V}$
2425	0	2	0	5	0.0	100.0	32.5
2400	2	2	2	3	40.0	60.0	7.5
2375	3	0	5	1	83.3	16.7	17.5
2350	1	1	6	1	85.7	14.3	42.5
2325	1	0	7	0	100.0	0.0	67.5

$\bar{V} = 2392.5$ volts

$n = 4$

$$\left[\frac{\Sigma(V_i - \bar{V})^2}{n(n-1)} \right]^{1/2} = 13.6$$

$u = 2392.5 \pm 43.3$ volts for 3 degrees of freedom

Table VI: Statistical analysis of data obtained in light ignition test with colloidal PbN₆ aged 17.5 minutes at 250°C with computed 50/50 voltage and 95% confidence level.

V_i	N	Y	ΣN	ΣY	% ΣN	% ΣY	$V_i - \bar{V}$
2525	0	1	0	7	0.0	100.0	50.0
2500	1	3	1	6	14.3	85.7	25.0
2475	2	3	3	3	50.0	50.0	0.0
2450	2	0	5	0	100.0	0.0	25.0

$\bar{V} = 2475$ volts

$n = 4$

$$\left[\frac{\Sigma(V_i - \bar{V})^2}{n(n-1)} \right]^{1/2} = 7.22$$

$u = 2475 \pm 22.95$ volts for 3 degrees of freedom

Table VII: Statistical analysis of data obtained in light ignition test with colloidal PbN₆ aged 20 minutes at 250°C with computed 50/50 voltage and 95% confidence interval.

V_i	N	Y	ΣN	ΣY	% ΣN	% ΣY	$V_i - \bar{V}$
2500	0	3	0	14	0	100.0	41.7
2475	3	6	3	11	21.4	78.6	16.7
2450	6	1	9	5	64.3	35.7	8.3
2425	0	2	9	4	69.2	30.8	33.3
2400	1	2	10	2	85.3	16.7	58.3
2375	2	0	12	0	100.0	0.0	83.3

$\bar{V} = 2458.3$ volts

$n = 14$

$$\left[\frac{\Sigma (V_i - \bar{V})^2}{n(n-1)} \right]^{1/2} = 8.26$$

$u = 2458.3 \pm 17.85$ volts for 13 degrees of freedom

Table VIII: Statistical analysis of data obtained in light ignition test with colloidal PbN₆ aged 30 minutes at 250°C with computed 50/50 voltage and 95% confidence interval.

V_i	N	Y	ΣN	ΣY	% ΣN	% ΣY	$V_i - \bar{V}$
2600	0	2	0	7	0.0	100.0	48.15
2575	1	4	1	5	16.7	83.3	23.15
2550	3	1	4	1	80.0	20.0	11.85
2525	1	0	5	0	100.0	0.0	36.85

$\bar{V} = 2561.85$ volts

$n = 2$

$$\left[\frac{\Sigma (V_i - \bar{V})^2}{n(n-1)} \right]^{1/2} = 18.4$$

$u = 2561.85 \pm 234$ volts for 1 degree of freedom

Table IX: Summary of statistical analysis data from sensitivity tests of colloidal PbN_6 various aging times with computed 50/50 voltage and 95% confidence interval by using light ignition test.

	50/50 Explosion Point	95% Confidence Interval
1. Non aged colloidal PbN_6	2356.2 volts	2356.7 ± 17.8 volts
2. Aged 5 minutes at 250°C	2207.15 "	2207.15 ± 34.8 "
3. Aged 10 minutes at 250°C	2320.6 "	2320.6 ± 22 "
4. Aged 12.5 minutes at 250°C	2408.3 "	2408.3 ± 35.6 "
5. Aged 15 minutes at 250°C	2392.5 "	2392.5 ± 43.3 "
6. Aged 17.5 minutes at 250°C	2375 "	2475 ± 22.95 "
7. Aged 20 minutes at 250°C	2458.3 "	2458.3 ± 17.85 "
8. Aged 30 minutes at	2561.85 "	2561.85 ± 234 "

Table X: Statistical analysis of data obtained in hot wire test with colloidal PbN_6 non-aged with computed 50/50 voltage and 95% confidence interval.

V_i	N	Y	ΣN	ΣY	% ΣN	% ΣY	$V_i - \bar{V}$
1.04	0	3	0	5	0	100.0	0.015
1.02	4	2	4	2	66.7	33.3	0.005
1.00	3	0	7	0	100.0	0.0	0.025

$$\bar{V} = 1.025 \text{ volts}$$

$$n = 2$$

$$\left[\frac{\sum (V_i - \bar{V})^2}{n(n-1)} \right]^{1/2} = 0.005$$

$$u = 1.025 \pm 0.0635 \text{ volts for 1 degree of freedom}$$

Table XI: Statistical analysis of data obtained in hot wire test with colloidal PbN₆ aged 5 minutes at 250°C with computed 50/50 voltage and 95% confidence interval.

V_i	N	Y	ΣN	ΣY	% ΣN	% ΣY	$V_i - \bar{V}$
1.09	0	1	0	6	0	100.0	0.02
1.08	1	2	1	5	16.5	83.5	0.01
1.07	2	2	3	3	50.0	50.0	0
1.06	2	1	5	1	83.5	16.5	0.01
1.05	1	0	6	0	100.0	0.0	0.02

$$\bar{V} = 1.07$$

$$n = 5$$

$$\left[\frac{\Sigma(V_i - \bar{V})^2}{n(n-1)} \right]^{1/2} = 0.01$$

$$u = 1.07 \pm 0.0278 \text{ volts for 4 degrees of freedom}$$

Table XII: Statistical analysis of data obtained in hot wire test with colloidal PbN₆ aged 10 minutes at 250°C with computed 50/50 voltage and 95% confidence interval.

V_i	N	Y	ΣN	ΣY	% ΣN	% ΣY	$V_i - \bar{V}$
1.11	0	1	0	7	0.0	100.0	0.0325
1.10	0	2	0	6	0.0	100.0	0.0225
1.09	1	1	1	4	20.0	80.0	0.0125
1.08	1	2	2	3	40.0	60.0	0.0025
1.07	2	1	4	1	80.0	20.0	0.0075
1.06	1	0	5	0	100.0	0.0	0.0175

$$\bar{V} = 1.0775 \text{ volts}$$

$$n = 4$$

$$\left[\frac{\Sigma(V_i - \bar{V})^2}{n(n-1)} \right]^{1/2} = 0.00137$$

$$u = 1.0775 \pm 0.0043 \text{ volts for 3 degrees of freedom}$$

Table XIII: Statistical analysis of data obtained in hot wire test with colloidal PbN₆ aged 15 minutes at 250°C with computed 50/50 voltage and 95% confidence interval.

V_i	N	Y	ΣN	ΣY	% ΣN	% ΣY	$V_i - \bar{V}$
1.14	0	4	0	6	0.0	100.0	0.0075
1.13	4	2	4	2	66.7	33.3	0.0025
1.12	2	0	6	0	100.0	0.0	0.0125

$\bar{V} = 1.1325$ volts

$n = 2$

$$\left[\frac{\Sigma (V_i - \bar{V})^2}{n(n-1)} \right]^{1/2} = 0.0025$$

$u = 1.1325 \pm 0.0317$ volts for 1 degree of freedom

Table XIV: Statistical analysis of data obtained in hot wire test with colloidal PbN₆ aged 20 minutes at 250°C with computed 50/50 voltage and 95% confidence interval.

V_i	N	Y	ΣN	ΣY	% ΣN	% ΣY	$V_i - \bar{V}$
1.15	0	2	0	10	0.0	100.0	0.035
1.14	1	2	1	8	11.0	88.0	0.025
1.13	1	2	2	6	25.0	75.0	0.015
1.12	1	1	3	4	42.8	57.2	0.005
1.11	1	1	4	3	57.2	42.8	0.005
1.10	1	2	5	2	71.4	28.6	0.015
1.09	2	0	7	0	100.0	0.0	0.025

$\bar{V} = 1.115$ volts

$n = 8$

$$\left[\frac{\Sigma (V_i - \bar{V})^2}{n(n-1)} \right]^{1/2} = 0.00626$$

$u = 1.115 \pm 0.0001$ volts for 7 degrees of freedom

Table XV: Statistical analysis of data obtained in hot wire test with colloidal PbN₆ aged 30 minutes at 250°C with computed 50/50 voltage and 95% confidence interval.

V_i	N	Y	ΣN	ΣY	% ΣN	% ΣY	$V_i - \bar{V}$
1.16	0	1	0	11	0	100.0	0.02641
1.15	1	4	1	10	9.1	90.9	0.01641
1.14	3	2	4	6	40.0	60.0	0.00641
1.13	1	1	5	4	55.6	44.4	0.00359
1.12	0	2	5	3	62.5	37.5	0.01359
1.11	2	1	7	1	87.3	12.7	0.02359
1.10	1	0	8	0	100.0	0.0	0.03359

$\bar{V} = 1.13359$ volts

$n = 10$

$$\frac{\Sigma(V_i - \bar{V})^2}{n(n-1)}^{1/2} = 0.004825$$

$u = 1.13359 \pm 0.0109$ volts for 9 degrees of freedom

Table XVI: Summary of statistical analysis of data from sensitivity tests of colloidal PbN₆ after various aging times with computed 50/50 voltage and 95% confidence interval by using hot wire test.

Date Dried	Date Aged	Date Tested	Aging Time	50/50 Voltage 95% Confidence Interval	Room Temperature Range during Testing °C
7/7/61	7/12/61	7/10/61	None	1.025 ± 0.0635	Temperature not recorded
7/7/61	7/12/61	7/18/61	5 min.	1.07 ± 0.0278	" " "
7/7/61	7/12/61	7/20/61	10 min.	1.0775 ± 0.0043	32°C
7/7/61	7/12/61	7/21/61	15 min.	1.1325 ± 0.0317	32-33°C
7/7/61	7/12/61	7/27/61 7/28/61	20 min.	1.1115 ± 0.0044	33-35.5°C
7/7/61	7/12/61	7/28/61	30 min.	1.13359 ± 0.0109	32-33°C

Table XVII: Statistical analysis of data obtained in light ignition test with colloidal PbN₆ (non-aged) with computed 50/50 voltage and 95% confidence interval.

V_i	N	Y	ΣN	ΣY	% ΣN	% ΣY	$V_i - \bar{V}$
2375	0	3	0	13	0.0	100.0	50.0
2350	3	4	3	10	23.1	76.9	25.0
2325	3	6	6	6	50.0	50.0	0.0
2300	5	0	11	0	100.0	0.0	25.0

$\bar{V} = 2325$ volts

$n = 9$

$$\left[\frac{\Sigma (V_i - \bar{V})^2}{n(n-1)} \right]^{1/2} = 5.1$$

$u = 2325 \pm 16.2$ volts for 8 degrees of freedom

Table XVIII: Statistical analysis of data obtained in light ignition test with colloidal PbN₆ aged under O₂ 26 days at 35°C with computed 50/50 voltage and 95% confidence interval.

V_i	N	Y	ΣN	ΣY	% ΣN	% ΣY	$V_i - \bar{V}$
2450	0	2	0	13	0	100.0	78.14
2425	2	3	2	11	15.4	84.6	53.14
2400	2	4	4	8	33.3	66.7	28.14
2375	3	4	7	4	63.6	36.4	3.14
2350	4	0	11	0	100.0	0.0	21.86

$\bar{V} = 2371.86$ volts

$n = 10$

$$\left[\frac{\Sigma (V_i - \bar{V})^2}{n(n-1)} \right]^{1/2} = 9.64$$

$u = 2371.86 \pm 21.8$ volts for 9 degrees of freedom

Table XIX: Statistical analysis of data obtained in light ignition test with colloidal PbN₆ aged under N₂ 26 days at 35°C with computed 50/50 voltage and 95% confidence interval.

V _i	N	Y	ΣN	ΣY	%ΣN	%ΣY	V _i - $\bar{V}$
2325	0	2	0	11	0.0	100.0	37.2
2300	2	7	2	9	18.2	81.8	12.2
2275	8	2	10	2	83.3	16.7	12.8
2250	3	0	13	0	100.0	0.0	37.8

$\bar{V} = 2287.8$ volts

n = 4

$$\left[\frac{\sum (V_i - \bar{V})^2}{n(n-1)} \right]^{1/2} = 7.2$$

u = 2287.8 ± 22.95 volts for 3 degrees of freedom

Table XX: Statistical analysis of data obtained in light ignition test with colloidal PbN₆ aged under air 26 days at 35°C with computed 50/50 voltage and 95% confidence interval.

V _i	N	Y	ΣN	ΣY	%ΣN	%ΣY	V _i - $\bar{V}$
2350	0	2	0	12	0.0	100.0	37.5
2325	2	8	2	10	16.7	83.3	12.5
2300	8	2	10	2	83.3	16.7	12.5
2275	2	0	12	0	100.0	0.0	37.5

$\bar{V} = 2312.5$ volts

n = 4

$$\left[\frac{\sum (V_i - \bar{V})^2}{n(n-1)} \right]^{1/2} = 7.21$$

u = 2312.5 ± 22.92 volts for 3 degrees of freedom

Table XXI: Statistical analysis of data obtained in light ignition test with colloidal PbN₆ aged under argon 26 days at 35°C with computed 50/50 voltage and 95% confidence interval.

V_i	N	Y	ΣN	ΣY	% ΣN	% ΣY	$V_i - \bar{V}$
2400	0	3	0	12	0.0	100.0	40.0
2375	3	5	3	9	25.0	75.0	15.0
2350	5	4	8	4	66.7	33.3	10.0
2325	4	0	12	0	100.0	0.0	35.0

$\bar{V} = 2360$ volts

$n = 7$

$$\left[\frac{\Sigma(V_i - \bar{V})^2}{n(n-1)} \right]^{1/2} = 5.06$$

$u = 2360 \pm 12.4$ volts for 6 degrees of freedom

Table XXII: Statistical analysis of data obtained in light ignition test with colloidal PbN₆ aged under O₂ 65 days at 35°C with computed 50/50 voltage and 95% confidence interval.

V_i	N	Y	ΣN	ΣY	% ΣN	% ΣY	$V_i - \bar{V}$
2400	0	3	0	14	0.0	100.0	79.59
2375	2	2	2	11	15.4	84.6	54.59
2350	1	3	3	9	25.0	75.0	29.59
2325	2	3	5	6	45.5	54.5	4.59
2300	2	2	7	3	70.0	30.0	20.41
2275	2	1	9	1	90.0	10.0	45.41
2250	1	0	10	0	100.0	0.0	70.41

$\bar{V} = 2320.41$ volts

$n = 14$

$$\left[\frac{\Sigma(V_i - \bar{V})^2}{n(n-1)} \right]^{1/2} = 9.07$$

$u = 2320.41 \pm 19.6$ volts for 13 degrees of freedom

Table XXIII: Statistical analysis of data obtained in light ignition test with colloidal PbN₆ aged under N₂ 65 days at 35°C with computed 50/50 voltage and 95% confidence interval.

V _i	N	Y	ΣN	ΣY	%ΣN	%ΣY	V _i - $\bar{V}$
2375	0	2	0	11	0.0	100.0	34.28
2350	3	8	3	9	25.0	75.0	9.28
2325	9	1	12	1	92.3	7.7	15.72
2300	1	0	13	0	100.0	0.0	40.72

$\bar{V} = 2340.72$ volts

n = 4

$$\left[\frac{\sum (V_i - \bar{V})^2}{n(n-1)} \right]^{1/2} = 6.49$$

u = 2340.72 ± 20.06 volts for 3 degrees of freedom

Table XXIV: Statistical analysis of data obtained in light ignition test with colloidal PbN₆ aged under air 65 days at 35°C with computed 50/50 voltage and 95% confidence interval.

V _i	N	Y	ΣN	ΣY	%ΣN	%ΣY	V _i - $\bar{V}$
2350	0	4	0	10	0.0	100.0	30.31
2325	5	2	5	6	45.5	54.5	5.31
2300	3	1	8	4	66.7	33.3	19.96
2275	2	2	10	3	76.9	23.1	44.69
2250	3	1	13	1	92.86	7.14	69.69
2225	1	0	14	0	100.00	0.0	94.69

$\bar{V} = 2319.69$ volts

n = 13

$$\left[\frac{\sum (V_i - \bar{V})^2}{n(n-1)} \right]^{1/2} = 8.96$$

u = 2319.69 ± 19.54 volts for 12 degrees of freedom

Table XXV: Statistical analysis of data obtained in light ignition test with colloidal PbN_6 aged under argon 65 days at 35°C with computed 50/50 voltage and 95% confidence interval.

V_i	N	Y	ΣN	ΣY	% ΣN	% ΣY	$V_i - \bar{V}$
2650	0	3	0	13	0.0	100.0	46.2
2625	3	4	3	10	23.1	76.9	21.2
2600	4	3	7	6	54.8	45.2	3.8
2575	2	3	9	3	75.0	25.0	28.8

$\bar{V} = 2603.8$ volts

$n = 12$

$$\left[\frac{\Sigma(V_i - \bar{V})^2}{n(n-1)} \right]^{1/2} = 5.47$$

$u = 2603.8 \pm 12.04$ volts for 11 degrees of freedom

Table XXVI: Statistical analysis of data obtained in light ignition test with colloidal PbN_6 aged under O_2 80 days at 35°C with computed 50/50 voltage and 95% confidence interval.

V_i	N	Y	ΣN	ΣY	% ΣN	% ΣY	$V_i - \bar{V}$
2400	0	2	0	14	0.0	100.0	64.6
2375	2	4	0	12	14.3	85.7	39.4
2350	3	3	5	8	38.7	61.3	14.4
2325	2	2	7	5	58.3	41.7	10.6
2300	1	2	8	3	72.7	27.3	35.6
2275	1	1	9	1	90.0	10.0	60.6
2250	1	0	10	0	100.0	0.0	85.6

$\bar{V} = 2335.6$ volts

$n = 10$

$$\left[\frac{\Sigma(V_i - \bar{V})^2}{n(n-1)} \right]^{1/2} = 11.6$$

$u = 2335.6 \pm 26.2$ volts for 9 degrees of freedom

Table XXVII: Statistical analysis of data obtained in light ignition test with colloidal PbN_6 aged under N_2 80 days at 35°C with computed 50/50 voltage and 95% confidence interval.

V_i	N	Y	ΣN	ΣY	% ΣN	% ΣY	$V_i - \bar{V}$
2375	0	3	0	12	0.0	100.0	35.7
2350	3	7	3	9	25.0	75.0	10.7
2325	7	2	10	2	83.4	16.6	14.3
2300	2	0	12	0	100.0	0.0	39.3

$\bar{V} = 2339.3$ volts

$n = 5$

$$\left[\frac{\Sigma(V_i - \bar{V})^2}{n(n-1)} \right]^{1/2} = 5.11$$

$u = 2339.3 \pm 14.2$ volts for 4 degrees of freedom

Table XXVIII: Statistical analysis of data obtained in light ignition test with colloidal PbN_6 aged under air 80 days at 35°C with computed 50/50 voltage and 95% confidence interval.

V_i	N	Y	ΣN	ΣY	% ΣN	% ΣY	$V_i - \bar{V}$
2375	0	1	0	13	0.0	100.0	61.0
2350	1	3	1	12	7.7	92.3	36.0
2325	2	7	3	9	25.0	75.0	11.0
2300	6	2	9	2	81.8	18.2	14.0
2275	2	0	11	0	100.0	0.0	39.0

$\bar{V} = 2314$ volts

$n = 6$

$$\left[\frac{\Sigma(V_i - \bar{V})^2}{n(n-1)} \right]^{1/2} = 8.27$$

$u = 2314 \pm 21.24$ volts for 5 degrees of freedom

Table XXIX: Statistical analysis of data obtained in light ignition test with colloidal PbN_6 aged in argon 80 days at 35°C with computed 50/50 voltage and 95% confidence interval.

V_i	N	Y	ΣN	ΣY	% ΣN	% ΣY	$V_i - \bar{V}$
2650	0	2	0	13	0.0	100.0	60.4
2625	1	3	1	11	8.3	91.7	35.4
2600	2	6	3	8	27.3	72.7	10.4
2575	6	2	9	2	81.8	18.2	14.6
2550	2	0	11	0	100.0	0.0	39.6

$$\bar{V} = 2589.6$$

$$n = 6$$

$$\left[\frac{\Sigma (V_i - \bar{V})^2}{n(n-1)} \right]^{1/2} = 8.16$$

$$u = 2589.6 \pm 21 \text{ volts for } 5 \text{ degrees of freedom}$$

 Table XXX: Summary of statistical analyses data from sensitivity tests on colloidal PbN_6 heat treated under different gases for various amounts of time at 35°C with computed 50/50 voltage and 95% confidence interval. (Sample all from same bottle of colloidal PbN_6)

Name of Sample	Test voltage of 50/50 point and 95% confidence interval
Standard colloidal PbN_6 (non-aged)	2325 ± 16.2 volts
Colloidal PbN_6 stored in O_2 26 days	2371.86 ± 21.8 volts
Colloidal PbN_6 stored in O_2 65 days	2320.41 ± 19.6 volts
Colloidal PbN_6 stored in O_2 80 days	2335.6 ± 26.2 volts
Colloidal PbN_6 stored in N_2 26 days	2287.8 ± 22.95 volts
Colloidal PbN_6 stored in N_2 65 days	2340.72 ± 20.06 volts
Colloidal PbN_6 stored in N_2 80 days	2339.3 ± 14.2 volts
Colloidal PbN_6 stored in air 26 days	2312.5 ± 22.92 volts
Colloidal PbN_6 stored in air 65 days	2319.69 ± 19.54 volts
Colloidal PbN_6 stored in air 80 days	2314 ± 21.24 volts
Colloidal PbN_6 stored in argon 26 days	2360 ± 12.4 volts
Colloidal PbN_6 stored in argon 65 days	2603.8 ± 12.04 volts
Colloidal PbN_6 stored in argon 80 days	2589.6 ± 21.0 volts

Table XXXI: Results of azide value for commercial lead azide and long-term treatments of colloidal lead azide,

Name of Sample	Azide Value	Remarks
Colloidal lead azide non-aged dried 7/29/61	95.4%	One trial
Colloidal lead azide aged at 250°C 2 hours	95.917%	"
Colloidal lead azide aged at 250°C 16 hours 18 minutes	77.99%	"
#1 lead azide milled 8 hours, Olin Mathieson #58-1	93.58%	"
#2 coarse lead azide Olin Mathieson #59-3	92.11%	"
#3 coarse lead azide DuPont #608	92.81%	"
#4 coarse lead azide DuPont #343	91.28%	"
Colloidal lead azide non-aged	93.38 $\pm$ 0.4%	Two trials
Colloidal lead azide in O ₂ 26 days at 35°C	98.33% $\pm$ 0.1%	"
Colloidal lead azide in O ₂ 65 days at 35°C	95.857% $\pm$ 0.25%	"
Colloidal lead azide in O ₂ 80 days at 35°C	97.30% $\pm$ 0%	"
Colloidal lead azide in N ₂ 26 days at 35°C	95.10% $\pm$ 0.3%	"
Colloidal lead azide in N ₂ 65 days at 35°C	93.271% $\pm$ 0.2%	"
Colloidal lead azide in N ₂ 80 days at 35°C	93.691% $\pm$ 0.45%	"
Colloidal lead azide in air 26 days at 35°C	95.22% $\pm$ 0.2%	"
Colloidal lead azide in air 65 days at 35°C	96.00 $\pm$ 0.5%	"
Colloidal lead azide in air 80 days at 35°C	93.54% $\pm$ 0.23%	"
Colloidal lead azide in air 26 days at 35°C	93.196% $\pm$ 0%	"
Colloidal lead azide in air 65 days at 35°C	96.452% $\pm$ 0.6%	"
Colloidal lead azide in air 80 days at 35°C	96.431% $\pm$ 0.22%	"

from that of the standard non-aged sample. The maximum in sensitivity shown by the light ignition test as a result of 5-10 minutes aging certainly must be real, since this agrees with previous findings using the miniature card-gap test⁽¹⁸⁾ (except that the sensitivity maximum occurred for slightly longer heat-treatment times) as well as those mentioned earlier with regard to the "memory effect" in thermal explosion. It is not known why the hot wire test did not show a similar sensitization as a result of partial decomposition. Perhaps this negative result was due to the past history of the lead azide. The samples used in the light ignition tests were aged at a different time than those to which the hot wire test was applied. Results obtained subsequent to these tests indicated that the past history of the lead azide may be an important factor, a fact which was not appreciated at the time the heat treatments were carried out. On the basis of this later information it would have been advisable to maintain better control of the untreated sample and to have tested the heat-treated lead azide immediately after aging because ambient conditions may affect the sensitivity.

In regards to the performance of the hot wire test, more scatter of the results was encountered than was desired, which required an excessive number of trials in order to determine the 50/50 point with an accuracy that would be sufficient to differentiate the rather small differences in sensitivity encountered in the experiments of this study. Most of the difficulty was believed to be the result of the hot wire not being sufficiently uniform in resistance along its length. Possibly if wire of precisely uniform diameter were available, the hot wire test would be more reproducible.

The sensitization of lead azide as a result of heat treatments at 250°C for 5-10 minutes that were observed to occur in the light ignition test and at the slightly later times in the modified card-gap test probably is associated in part with the growth of lead specks on the surfaces of lead azide. Electron micrographs obtained by Head⁽¹⁰⁾ showed that lead specks were formed on lead azide crystal surfaces during decomposition and that as decomposition proceeded these lead specks grew in size. In addition, each speck was observed to lie in a crater showing, therefore, a collapse of the

lead azide lattice in the vicinity of each lead speck. On the basis of this lead speck growth and the corresponding crater formation a semiconductor mechanism for the thermal decomposition of lead azide was proposed according to which the formation of nitrogen by the combination of two positive holes with the release of heat was said to occur primarily at the lead specks. Such a mechanism could explain the autocatalytic behavior of lead azide in thermal decomposition and some increase in sensitivity as a result of partial decomposition because of the increased likelihood of hot spot formation as a result of the more rapid decomposition.

The concentration and types of "active centers" might be expected to influence the sensitivity of lead azide due to the fact that lead azide decomposes by an electron transfer process. Under such circumstances the photoconductivity or the dark conductivity should be related in some manner to the sensitivity. Rollins, et. al.⁽¹⁹⁾ in measurements of the photoconductivity of lead azide found that the photoconductivity in the 406 mμ band increased markedly as the time of heat-treatment at 250°C was increased. Since the wavelength of light used was too long for photolysis to occur, these results were first interpreted to mean that the electron donating centers were lead specks which formed on the crystal surfaces during decomposition. In later work of Rollins, et. al.⁽²⁰⁾ (see the previous section) where the lead azide was heat treated in a more efficient manner and photoconductivity measurements were performed immediately after the heat-treatment, it was found that photocurrents could not be measured above the high dark current background. The dark current in this case was found to exhibit a maximum corresponding to 10-15 minutes heat treatment, and with further treatment it dropped to about the value for the untreated lead azide. When samples were heat-treated at 100°C instead of 250°C, the dark current was lower, and photocurrents could be measured. Surprisingly the shapes of both the latter curves were similar to the former curve with maxima occurring at 10-15 minutes treatment times. These results certainly appear to bear a relationship to the effect of heat treatments upon sensitivity in which a sensitivity maximum was observed for about the same length heat treatment. The fact that the sensitivity was found to be a

maximum for 5-15 minutes aging at 250°C indicates that lead speck growth must not be the only factor affecting the sensitivity as a results of heat treatments. Otherwise the sensitivity would be expected to increase for considerably longer heat-treatment times along with the corresponding continued lead speck growth until perhaps the azide content of the sample had been depleted sufficiently to lower the sensitivity. This phenomenon, would not be expected to occur in 5-15 minutes because the amount of decomposition at 250°C for this amount of time would be too small. This point is in agreement with a conclusion of reference (20), summarized in Section IV, that active centers other than colloidal centers must be produced by heating, and interactions must occur after 10-15 minutes which tend to annihilate the centers. In the study of reference (20), however, two temperatures namely, 250°C and 100°C were used, and the 10-15 minutes time period involved appeared to be independent of the temperature within this range. The sensitivity tests were made only for treatments at 250°C, however.

B. Long Term Aging Treatments at 35°C in Various Atmospheres

Upon examination of the lead azide value data listed in Table XXXI for the long-term aged lead azide, the standard non-aged lead azide and various other samples of lead azide, one will note firstly that the samples aged in nitrogen, oxygen, and air tended to possess higher lead azide values than the standard non-aged sample. However, there existed some unexplained inconsistencies in the case of nitrogen and air where after 80 days aging the lead azide content dropped to about the original value of the standard sample after showing an increase for shorter aging times. The increased lead azide content indicated by the assays was attributed to be due to some of the free lead, otherwise in the lead azide, combining with the atmosphere particularly in the case of oxygen to form compounds that would react in the titration to indicate a higher lead azide value than was actually the case. This possibility was substantiated by the fact that $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ solution readily dissolved lead oxide. With the nitrogen atmosphere possibly the lead azide content might actually be increased, or again, compounds with the free lead, primarily nitrides, might form which would dissolve during the titration such to contribute to

the apparent lead azide content. At present little is known regarding either of these possibilities. In either event it is difficult to explain why the lead azide determinations indicated a drop in azide content after 80 days aging in air and 65 days aging in nitrogen when initial increases were exhibited.

No reason for the increase in the apparent lead azide content after 26 days aging in argon can be advanced at this time. The possibility exists that the determinations were in error. However, this is not likely considering the care that was exercised in making the determinations and the good agreement that was obtained between duplicate determinations.

Comparison of the lead azide assay data listed in Table XXXI with the 50/50 go-no go data for the light ignition test given in Table XXX shows no correlation between the apparent lead azide content and sensitivity. The light ignition test did not prove sufficiently sensitive to show any significant differences in sensitivity between the standard samples and the samples aged for 26, 65, and 80 days in nitrogen, oxygen, and air. However, after 65 days and 80 days aging in argon, the sensitivity to ignition by light was found to be reduced significantly, the 50/50 point with its 95% confidence interval after 26 days being $2360 \pm 12.4V$ (which was slightly higher than the non-aged sample), but after 65 days having jumped to $2603.8 \pm 12.04 V$. The above results are especially interesting when correlated to photoconductivity measurements of Rollins, et. al.⁽²⁰⁾ and electron micrographic surface examinations performed by Thornley, et. al.⁽²¹⁾ both summarized in earlier sections of this report. The photoconductivity of lead azide, which as pointed out earlier is believed to be related to its sensitivity, was found to be affected in a reproducible manner by the atmosphere surrounding the lead azide, the nitrogen-treated sample having the highest photoconductivity, followed by the air treated, the oxygen treated, and the argon treated samples. Photoconductivity apparently is a much more sensitive test, however, than the light ignition test for sensitivity because only in the case of the argon treatment did this test show a significant difference as a result of the treatments. Of further significance is the fact

that the photocurrent of the nitrogen treated samples could be progressively reduced simply by placing these samples in a vacuum.

Thus, it appears that exposure to certain gases, especially nitrogen, leads to diffusion of the gas into the lead azide lattice with the subsequent formation of active centers which contribute to photocurrents and also affect the sensitivity. In the case of the argon treatment the argon would not be expected to produce active centers. However, certain active centers already in the lead azide, in this instance might be expected to diffuse to the surface with the consequent lowering of the photoconductivity and the sensitivity.

Surface examinations of lead azide crystals performed by Thornley, et. al. ⁽²¹⁾ using electron microscopy have shown the surfaces to be altered significantly by the atmospheric environment. It thus seems evident in view of this fact and the above results that the characteristics of a given lead azide are determined to quite an extent by the past history of the lead azide. It is quite likely that some of the effects occur quite rapidly, such as the diffusion of nitrogen from the atmosphere into the lattice to form active centers. As yet no tests have been performed on lead azide which has never been exposed to air or lead azide which has been stored in a vacuum. One would expect on the basis of the results with argon that in both cases the sensitivity would be lower.

VI. Reaction of Carbon Dioxide and Water Vapor With Lead Azide

From the study of reference (21), which was summarized in Section II, the fact was determined that the presence of water vapor and carbon dioxide affected the surface topography of α -lead azide. Since carbon dioxide and water are a part of the normal environment in which lead azide is stored, it in fact generally being stored under water, the present study was initiated. The purposes of the investigation were to determine the mechanism of reaction of carbon dioxide and water vapor with lead azide, to ascertain the conditions under which surface compounds would form, and to identify the nature of the surface components. The results of this investigation have been given in a technical report whose title is the same as this section. Hence only a summary will be included here.

Briefly, the procedure was to treat either lead azide crystals or colloidal lead azide in the desired manner. Then observations of surface changes produced were made by electron microscopy, and the identification of possible reaction products was accomplished by infrared spectrophotometry. The electron microscopic observations were confined to crystals, applications of this method to colloidal lead azide proving to be unsuccessful. Carbon replica techniques were employed to obtain the electron micrographs. An inherent property of the replicating technique is that in addition to yielding an "imprint" of the crystal surface foreign material present on the surface frequently adheres to the replica film producing what is known as an extractive replica. This fact then provides a very sensitive method for detecting surface compounds foreign to lead azide provided such compounds are not dissolved from the replica when the lead azide is dissolved away. This method in fact will show surface compounds when the concentrations are much too small to be detected by infrared spectrophotometry. The infrared spectra were obtained by pressing 1-2 mg of lead azide into a 200 mg KBr pellet and running it against a pure KBr pellet in a dual beam spectrophotometer.

The lead azide was treated about 50 mg. at a time in a small specially-constructed tube furnace which could be elevated to a specified, controlled temperature and through which gases could be circulated around the lead azide and thence out through an exit. The incoming gases were passed through an orifice prior to reaching the lead azide which practically eliminated any upstream diffusion of gaseous products from the lead azide, the treatment gases consisted of mixtures of CO_2 and water vapor (the wet CO_2 mixtures were produced by bubbling the CO_2 through water before entering the tube furnace, the concentration of water vapor being controlled by the temperature of the water), dry CO_2 , and H_2O vapor mixed with argon as a carrier gas.

A summary of the wet CO_2 treatments that were carried out along with remarks regarding their effects as assessed from electron micrographs of replicas of the crystal surfaces and from infrared spectrograms is given in Table XXXII. Examination of Table XXXII shows: (1) The extent of reaction of the lead azide with CO_2 water vapor (as indicated by the amount

of extracted foreign material on the carbon replicas) increased with the tube furnace temperature, the water bath temperature, and the treatment time. (2) The reaction products were carbonates, and (3) the electron micrographs provided a much more sensitive means for detecting surface compound formation than did infrared absorption spectrophotometry.

That appreciable amounts of surface carbonates could form under ambient conditions during long periods of time was illustrated by the results with a sample of colloidal lead azide which was stored at 30°C for 26 days in dry CO₂ and then for 24 more days in CO₂ and water vapor, which represented a total time of 50 days under conditions not greatly different than might be experienced in normal storage. Infrared spectrograms of this treated sample clearly showed the 7.2, 12, and 15 μ absorption peaks resulting from surface carbonates.

The fact that carbonates apparently form on lead azide surfaces to any appreciable extent only if water vapor is present with the CO₂ was shown by a second type of experiment in which relatively dry CO₂ directly from the cylinder was used. In this case after 64 hours exposure at 100°C electron micrographs indicated only a slight amount of reaction products and nothing was shown by infrared spectral analyses. As will be seen later such small amounts of surface reaction under the above condition are consistent with the proposed mechanism of carbonate formation.

According to Reitzner⁽²⁾ heating lead azide in the presence of water vapor produces a reaction which generates HN₃ and basic lead azide namely,

The above reaction was confirmed at this laboratory by treating lead azide in the tube furnace with wet argon. In one type of experiment the exit gases were bubbled through a silver nitrate solution. A white precipitate was formed, which according to its infrared absorption spectrum was an azide, indicating that the exit gases contained hydrazoic acid vapor. In a second experiment some of the exit gases were captured in an infrared gas cell and were subjected directly to infrared analyses. Again the absorption spectrum showed azide bonding.

Table XXXII: Summary of the CO₂-Water vapor treatments and the effect they produced.

Tube Furnace Temperature	Water Bath Temperature	Range of Treatment Times	Remarks
50°C	24°C	8-14 hours	Little if any alteration of the crystal surface topography occurred even after the longest treatment time.
70°C	24°C	2 1/2 - 25 hrs.	Electron micrographs showed small amounts of surface compound formation which increased with treatment time. Infrared spectrograms of the 25 hr. treated produce showed only the azide peak at ~ 5μ and the water peak at ~ 2.9μ.
90°C	24°C	4-20 hours	Electron micrographs showed a greater tendency for surface compound formation than previous tests. Infrared spectrograms again showed only the azide peak and the water peak.
90°C	60°C	3-16 hours	Electron micrographs indicated earlier and more pronounced surface compound formation.
100°C	60°C	2-52 hours	Electron micrographs showed very marked surface compound formation which increased stepwise with treatment time. After the 52 hour treatment an infrared spectrogram showed absorption peaks at ~ 7.2, 12, and 15μ due to carbonates as well as the 5μ azide peak and the 2.9μ water peak.
120°C	78°C	16 hours	Infrared spectrograms showed greater amounts of carbonates than previously.

In view of the fact that surface carbonates formed on lead azide in the presence of CO_2 and water vapor but did not appear to form without water vapor, the surface carbonate was thought to be lead carbonate created by the reaction of CO_2 with the PbO portion of the basic lead azide, the latter being created by the reaction of water vapor with lead azide as per the reaction given in equation (13). To test this conclusion commercial PbO was treated with dry CO_2 and wet CO_2 . In both cases the infrared absorption spectrum of the treated residue showed the presence of carbonates. As a reference check the absorption spectrum of commercial lead carbonate was run, and it proved to have peaks corresponding to those associated with carbonate formation on lead azide.

In conclusion the first step in the formation of carbonate is the formation of basic lead azide by the reaction of lead azide with water vapor as expressed by equation (13). The exact ratio of the lead oxide to the lead azide was not determined in the study but it probably varied with depth as the reaction proceeded into the crystal. It is known that there is a certain amount of free lead on the surface of lead azide and this could also react with water to form lead oxide.

However, reaction (13) most likely accounts for most of the PbO . The PbO is apparently the site for the CO_2 attachment because no carbonates were observed to form on lead azide unless a reaction had first taken place to form basic lead azide, and CO_2 was observed to react with commercial lead oxide to form lead carbonate. The small amount of carbonate formed when lead azide was treated with dry CO_2 may be attributed to exposure and adsorption of water and subsequent PbO formation which invariably would occur during the history of the azide.

The second step in the formation of carbonate on the lead azide is therefore the attachment of CO_2 to the PbO group in the basic lead azide, the net reaction represented by:

Since lead oxide in the presence of water vapor forms Pb(OH)_2 , in the presence of an excess of water reaction (13) may continue on to yield

in which case there would be an acid base reaction with carbonic acid present in the carbon dioxide-water vapor mixture

It is possible also for the CO_2 to react directly with the $\text{Pb(N}_3)_2 \cdot \text{Pb(OH)}_2$ to form the carbonate

Because of the complication introduced in the infrared absorption spectrum by the presence of water, it was not established that lead azide treated with water contained lead hydroxide. On the other hand no evidence was obtained that this compound did not exist. It was concluded, however, that the net reaction for lead azide with CO_2 and water vapor was

The intermediate steps may be entirely via equation (13). (This reaction certainly occurs because HN_3 is one of the products) and equation (15) or by a combination of the above and equations 16, 17, and 18. Temperature conditions may favor one of the paths. The fact that carbonates were detected in lead azide that had been stored in a carbon dioxide and water vapor environment at 30°C indicates that at least one of the mechanisms is involved at approximate storage temperatures.

The direct conclusions are that water does not represent an ideal storage environment for lead azide, because the presence of water tends to promote surface compound formation that in turn may affect the initiation reliability of lead azide.

VII. The Effects of Certain Accelerated Treatments Upon the Sensitivity of Lead Azide

The purpose of this phase was to determine if the sensitivity of lead azide was altered by various short-term treatments that were carried out

under more extreme temperature or pressure conditions than the long-term treatments described in Section V which were performed at nearly ambient temperatures and pressures. The treatments were essentially of two types namely (1) exposure to dry CO_2 or CO_2 and water vapor at elevated temperatures and ambient pressure and (2) exposure to nitrogen at elevated temperatures and ambient pressure and ambient temperature and elevated pressures. On the basis of results described in Sections IV, V, and VI these gases appeared to offer interesting possibilities for investigation. Following the treatments the samples were subjected to sensitivity determinations by the light ignition method, and the results were compared with those from a control. The light ignition test was chosen because it represented the most convenient test available upon which to base a survey of the effects of the treatments. The test is quite reproducible compared to most other means for determining sensitivity, and only small amounts of material are required for making a determination.

Prior to and during the experimental work a number of improvements were made on the equipment and experimental techniques in an effort to improve the accuracy and reproducibility of the results. As the work progressed experience with the procedures and results indicated that some of the earlier conclusions were incorrect. This summary presents a review of the results with the advantage of an overall picture of the work available, thereby providing a means of correcting any misinterpretations of results given in any of the monthly reports.

Control runs were made on air-dried samples of lead azide which resulted in the following 50/50 points expressed in terms of $V_i - V_f$ where V_i is the initial voltage of the capacitor which discharged across the spark gap and V_f is the residual voltage after discharge

15 days after drying 2850 volts

45 days after drying 2000 volts

This same sample, when exposed to N_2 for 48 hours (52 days after initial drying) at 150°C and ambient pressure also had a 50/50 go-no go voltage of 2000 volts, indicating no change from the 45-day result. In addition a second air-dried control sample tested at 2050 volts 56 days after drying.

The foregoing results appeared erratic with no trend evident as a consequence of the N_2 aging at elevated temperature. It was felt that perhaps the dryness of the sample had an effect upon the sensitivity, and a dessicator was obtained to check out this variable. A new sample had a 50/50 point of 2350 volts immediately after 4 days of air drying. A portion of this same sample was then desiccator-dried for 3 1/2 days with the result that the test voltage dropped to 2250 volts, thus indicating a slight increase in sensitivity which would be expected of a drier sample. A third portion of this same sample after being treated for 90 hours with N_2 at $150^\circ C$ and atmospheric pressure had a test voltage of 2275 V, which was not significantly different from the desiccator-dried sample and, therefore, indicated no effect on sensitivity from N_2 aging at elevated temperatures.

A second series of tests was conducted to determine effects of CO_2 on the sensitivity of lead azide. A desiccator-dried control sample was found to have 50/50 point of 2250 volts. Another portion of this sample was treated with CO_2 at $150^\circ C$ and atmospheric pressure for about 60 hours, after which it exhibited a 50/50 point of 3350 V, indicating a large reduction in sensitivity. A third portion of this sample was treated with H_2O -saturated CO_2 for 30 hours; then since the sample was too wet to test, it was held at $150^\circ C$ in air for another 30 hours. The resulting 50/50 point was 2525 volts, showing also a drop insensitivity when compared to the control although not so large as for the previous treatment. Since loss of sensitivity was attributed to the formation of carbonates on the azide surfaces, and the extent of such formation has been found to increase with increased concentrations of water vapor, it was felt that a re-run should be made because the experimental changes in sensitivity were less with the wet CO_2 treatment. Dry CO_2 was passed over another portion of the same sample at $150^\circ C$ for 98 hours, and this resulted in a 50/50 point of 2550 volts which was essentially the same as the CO_2 - H_2O treated sample, and considerably more sensitive than the first dry CO_2 test. The only difference between the first and second experiment involving

dry CO_2 was the time interval between treatment and testing. In the first case the sample was tested as soon as it cooled sufficiently to handle, while in the second case there was a 3-hour interval between treatment and testing. It thus appeared that some type of reverse reaction took place upon removal from the CO_2 environment, so that the low sensitivity evident immediately after treatment gradually increased to a higher value.

This phenomenon would also account for the results with the CO_2 - H_2O treated sample, for which the sensitivity surprisingly was reduced less than with the dry CO_2 treatments. Immediately after the wet CO_2 treatment the sample was too wet to make any significant sensitivity check. Hence it was dried in air at an elevated temperature for 30 hours during which time the postulated reverse reaction could have taken place bringing the sensitivity back to the same level as the second dry CO_2 test which had only a 3 hour time interval at ambient temperature between treatment and testing. Further evidence of this trend towards gradually recovering sensitivity upon exposure to air was apparent from another test made upon the same sample used for the second dry CO_2 test (2550 V). A portion of this sample (after being exposed to dry CO_2 for 89 hours) was placed in the dessicator for 4 days and then subjected to the light ignition test. The test voltage was 2300 volts, just 50 volts over the original control run.

It is unfortunate that time limitations did not permit the carrying out of additional tests to confirm the above findings. Certainly, the changes in sensitivity induced by the CO_2 - H_2O treatments were real because they were so large. Sufficient amounts of lead carbonate formed on the lead azide surfaces, would as mentioned previously, be expected to alter the sensitivity to initiation. However, the lead carbonate would be stable and, therefore, changes in sensitivity produced by its formation should not diminish during storage in air, indicating that additional affects were imposed by the treatments. What these affects were is not known at present. On the basis of results given above certainly further investigation of this problem is warranted. As is generally the case for treatments more than one factor apparently was affected which complicated the understanding of the phenomenon.

All tests to this point were made with 1/4" diameter 60° conically-tipped mild steel electrodes, and one set of electrodes was used for several discharges; however, the electrode gap was adjusted to 2 mm prior to each shot, and newly-machined electrodes were used more often as the go-no go voltage was being approached. In the last series of shots it was noted that replacement of used electrodes with newly-machined ones resulted in detonation of a test sample at the same voltage which had resulted in failure in the preceeding shot with used electrodes. Therefore, a check was made on the effect of eroding electrode tips. It was found that 60° conical-tipped electrodes experienced 0.003" longitudinal shortening for each discharge, while hemispherically-tipped electrodes (of the same 1/4" diameter mild steel material) were shortened by only 0.001" per discharge.

Tests were next made using hemispherically-tipped electrodes, and in one series it was found that failures occurred with voltages as high as 3000 volts when utilizing a set of used electrodes, while detonation occurred at voltages as low as 2750 volts when newly-machined electrodes were used. It was thus apparent that even with hemispherically tipped electrodes the change in the tips due to electrical discharge altered the arc characteristics sufficiently to effect significantly the test results. Roughening and blunting of the electrode tips apparently slowed the rate of radiant energy absorption by the azide sample. This resulted in failures at voltages which caused detonation when newly machined electrodes were used. Hemispherically tipped electrodes appeared to be affected in this way even more than the conically-tipped ones. As a final check, two control runs were made with the two types of electrodes on the same lead azide sample. The 50/50 point from the hemispherically-tipped electrodes was 2725 volts, while that for the conically-tipped electrodes was 2300 volts. Discharge from the sharp points of the latter type resulted in a higher rate of discharge than from the hemispheres of the former type, thereby causing initiation at a lower voltage. It was, therefore, decided to use a newly-machined set of conically-tipped electrodes for each shot on the ensuing runs.

The following runs constitute the tests in which lead azide samples were subjected to overpressures of nitrogen at ambient temperatures. The first control sample had a 50/50 point of 2320 volts. A portion of this sample was then subjected to an overpressure of nitrogen for 265 hours; at the beginning of the exposure the nitrogen pressure was 1310, psig and this gradually decreased to 980 psig at the end of the run (due to a small leak). The 50/50 point for this sample was 2625 volts indicating an appreciable decrease in sensitivity.

Another control run was next made on a newly dried sample resulting in a 50/50 point of 2225 volts. A portion of this sample subjected to a nitrogen overpressure of 500 psig for 15 minutes had a 50/50 point of 2600 volts-again indicating a significant reduction in sensitivity. Because of the apparent change in sensitivity resulting from the 15 minutes treatment a number of tests were carried out for treatments in this neighborhood of time. The next sample was subjected to a nitrogen overpressure of 500 psig for 30 minutes, and it had a 50/50 point of 2250 volts, indicating no significant change in sensitivity. Another sample subjected to an overpressure of 500 psig for 5 minutes, showed a 50/50 point of 2275 volts, and the next sample held at the same pressure for 10 minutes had the same 50/50 point. Finally the 500 psig--15 minute run was repeated and a test voltage of 2325 volts resulted. Another control run was then made on this batch of azide and a test voltage of 2250 volts resulted which was just slightly higher than the previous control run which yielded 2225 volts. Then another run at 200 psig for 15 minutes was made and this had a 50/50 point of 2350 volts.

Aside from the 235-hour exposure and the first 15-minute 500 psig run, there was very little change in sensitivity resulting from these tests. In an effort to ascertain whether or not there was any real change in lead azide sensitivity as a result of nitrogen overpressure, two more runs were made, and extreme care was taken to duplicate conditions existent when a change in sensitivity was indicated. The control run for this series had a 50/50 point of 2225 volts. A portion of this

sample was subjected to a nitrogen overpressure of 500 psig for 15 minutes and tested immediately afterwards; the resulting 50/50 point was 2500 volts. Finally, another portion of this initial sample subjected to the same pressure for 5 minutes had a 50/50 point of 2300 volts. These variations were not significant enough to indicate any trend in sensitivity change. It must, therefore, be concluded that subjecting lead azide to overpressures of nitrogen at ambient temperatures did not result in any significant changes in ignition sensitivity over the ranges tested in this experimentation, with the possible exception of the 265 hour exposure at relatively high pressure. And since the latter results were of the same order of change as the irreproducible result for the 15-minute 500-psig treatment even this change is open to question. The nitrogen used according to the manufacturer, was of very high purity. However, possibly it contained some water vapor, the presence of which could lower the sensitivity and would of course complicate the results. In view of the photoconductivity results given in Section IV, it was expected that if anything the nitrogen overpressure treatments would increase the sensitivity.

VIII. Growth of Lead Azide Crystals

Because of the constant need for crystals of the proper type in the electron microscopy experiments and in certain other phases of the investigations, the growing of lead azide crystals was continued during most of the contract period using the hydrazoic acid vapor diffusion method.⁽²²⁾ Attention was given to the cleanliness of the growing apparatus and the purity of the growing solutions, both of these factors being important for the production of well-formed crystals. A constant temperature bath was constructed which maintained the temperature of the growing solution to within a one degree daily variation rather than an approximately six degree variation which had prevailed previously. This closer temperature control led to some improvement in crystal size but not in crystal purity. A warmer temperature produced crystals faster, consequently with less surface absorption of impurities on the growing crystal faces. However, at

higher temperatures the crystals also apparently re-dissolved faster in the lead nitrate growing solution. Hence at each temperature there is an optimum rate of hydrazoic acid vapor diffusion required to produce satisfactory yields and crystals of good quality and maximum size. Optimizing all of the many parameters in the growing of lead azide crystals is a difficult task, and it is likely that an extended research project would be required in order to even hope to accomplish such an aim. In our studies the hydrazoic acid vapor concentration above the growing solution was increased from the 4% value normally used and greater yields resulted with the higher concentrations. (There is an upper limit to the hydrazoic acid vapor concentration which may be used due to its tendency to explode simultaneously at concentrations approaching 18%). That greater yields should occur can be seen from the equation for the reaction of hydrazoic and vapor with lead nitrate, namely,

The nitric acid produced in this reaction tends to dissolve the lead azide. However, increased concentrations of hydrazoic acid shift the equilibrium to the right. Vibration of the apparatus was also found to be an important factor. It tended to cause the crystals which normally grow on the surface of the lead nitrate solution to sink to the bottom where their growth rate would decrease and their rate of re-dissolving would increase.

The concentration of the lead nitrate solution was varied from 10% to a saturated solution which would run about 35%. The total yield was not varied to any great extent, except with the saturated solution, in which case the yield jumped by a factor of 10-15 times. The resulting crystals were very large and almost square in dimensions. They, however, proved to be crystals of lead nitrate, containing some lead azide as a impurity.

Since nitric acid formed in the reaction shown by equation (20) tended to dissolve the lead azide crystals limiting the yield, efforts were directed to eliminate the formation of nitric acid through the

use of salts of a different anion. The salts chosen were lead chloride and lead perchlorate. Particularly interesting results were obtained with lead chloride. The most obvious change brought about by the use of this salt was the increased yield which was roughly 10 times that experienced with lead nitrate solutions. The resulting crystals had the appearance of lead azide, and they decomposed in ceric ammonium nitrate with an evolution of nitrogen similar to azide grown in a nitrate medium. However, they were considerably less sensitive than the nitrate-grown (α n) crystals. Upon the performance of a lead azide assay of the chloride-grown (α c) crystals by the cerate oxidimetry method the azide content was found to be only about 51.5% whereas the normal α n crystals assayed generally at about 99.6%. The utilization of the lead chloride growing solution appeared, therefore, with the proper adjustment of conditions, to offer a means of varying the lead azide content at will with a consequent variance in sensitivity. In attempts to accomplish this firstly, the concentration of the lead chloride solution was varied. This proved to affect the yield but not the azide value. For example, using a saturated lead chloride solution, the α c crystal yield was 65 mg whereas under similar circumstances, but using a 50% saturated solution the yield dropped to 30 mg. In both cases, however, the lead azide value was assayed to be 51.4%. In further tests mixtures of saturated lead chloride solution and 10% lead nitrate solution were used in varying proportion. These proportions were varied from one part lead nitrate solution and 30 parts lead chloride solution to equal parts of each solution. Again only the crystal yield was affected. The extremes of the assays for the lead azide value were 51% to 51.9% which could not be construed to be significantly different within the accuracy of the method.

X-ray diffraction studies of α c crystals showed a distorted lead azide lattice, and there were no peaks corresponding to the chloride ion. Apparently then the chloride ion assumed azide lattice positions. The above results indicate that whenever lead chloride was present in the growing solution a new compound was produced having the composition $(\text{PbN})_{6/6}^{0.189} (\text{PbCl})_{2/2}^{0.162}$.

Yields considerably above those obtained with lead nitrate solutions were also realized using lead perchlorate. However, with this solution it was expected that the anion would be too large to occupy the azide position in the lattice. That this tendency existed was shown by the lead azide assay which proved to be approximately 97%. The αp or lead perchlorate-grown lead azide crystals possessed the same morphology as the standard αn crystals. Their color varied, however, from light green to yellow through black. Preliminary light ignition tests indicated that the αp crystals were of the same order of sensitivity as those grown from the nitrate solution.

The above limited experiments using the three lead salts showed that anion impurities could be taken into lead azide during crystal growth to a small or large extent depending upon the nature of the anion. These anion impurities may influence the sensitivity to a great extent as was the case for the αc crystals where the concentration of impurity was large. Or conceivably the effects may be more subtle where small impurity concentrations are involved. It should be pointed out that sufficiently accurate tests were not carried out to detect any small differences in sensitivity that might exist between αn and αp crystals. The tests ideally should be performed with single crystals because of the small sample sizes available and because crystal size is an important variable. Preliminary work showed that by selecting crystals falling within a fairly close size range, reproducible determinations of sensitivity could be made upon single crystals using the light ignition test. However, a careful comparison was never carried out between αp and αn crystals for example. In fact, there exists a whole realm of study concerning the effects of anion and cation impurities upon sensitivity, a field which was barely touched upon in our investigations. Described below are the few results obtained in connection with cation impurities.

Various metal nitrates comprising chromium, aluminum, barium, cobalt, and strontium were added to growing solutions in attempts to incorporate the cations in the lead azide lattice and possibly change the sensitivity and the growth properties of the crystals. Difficulties

were encountered in determining the amounts of these ions present in the grown crystals. For cobalt it was found that when the growing solution contained more than 300 parts per million (300 cobalt cations per million lead cations) the growth of lead azide crystals was almost completely suppressed. As the concentration of cobalt was decreased the lead azide yield increased until at 100 parts per million the yield was essentially the same as with pure lead nitrate solution. Emission spectrograms showed the presence of cobalt in the decomposition residue, although success was not achieved in determining the concentration. In the cases of chromium, aluminum and barium definite proof was not obtained that the cation was taken into the lead azide.

The lattice parameters of strontium azide and lead azide are quite similar as shown below.

<u>Azide</u>	<u>a(Å)</u>	<u>b(Å)</u>	<u>c(Å)</u>	<u>Reference</u>
$\alpha\text{-Pb}^{++}$	11.34	16.25	6.64	23
Sr^{++}	11.82	11.47	6.08	24

Hence the possibility existed that strontium would readily enter the lead azide lattice. Since some of the more ionically bonded azides tend to be less sensitive to shock, the incorporation of strontium impurity appeared to offer a means of varying the sensitivity of lead azide. In order to test this possibility lead azide crystals were grown in lead nitrate solutions containing small amounts of strontium nitrate. Concentrations of strontium ion in the growing solution ranged from 100 to 33,000 parts per million parts water by weight. Growth was suppressed in solutions of 33,000-16,000 ppm strontium. According to emission spectrograms of the decomposition residue only trace amounts of strontium occurred in lead azide grown in lead nitrate solutions containing 100 ppm strontium ion, and larger amounts were taken in when growing solutions richer in strontium ion were used. The maximum amount of strontium impurity which could be incorporated in the lead azide crystals was not determined during the contract period.

Samples of lead azide grown with strontium impurity were heated to detonation in a vacuum. Freshly grown crystals heated in a vacuum detonated in the 313° - 315°C range. The same batch of crystals were stored open to the atmosphere for a week at room temperature with minimum exposure to light. At the end of this period the minimum temperature for detonation has risen to 341° - 353°C . Crystals stored in plastic bottles in the dark detonated at 303° - 320°C . These results showed that the presence of strontium affected the sensitivity of lead azide since standard lead azide usually detonates at about 265°C . The whole problem of intentionally introduced impurities, their tendency to be taken into lead azide crystals, and their influence upon crystals morphology and upon sensitivity is a very interesting and worthwhile problem which was actually only surveyed briefly during the contract.

IX. Summary

Though there are a great number of questions that remain to be answered, it appears at this stage of the investigations that some of the effects that were heretofore puzzling, partially because a number of phenomenon were occurring simultaneously, are beginning to be sorted out and identified. Electron microscopic examinations of lead azide crystal surfaces for varying amounts of thermal decomposition (after the autocatalytic stage was established) confirmed the "semiconductor" mechanism for the thermal decomposition of lead azide, in which decomposition is accompanied by the growth of lead specks on the crystal surfaces. In addition each lead speck was found to lie in a crater that grew in size as the lead speck grew. This indicated that the combination of positive holes to form nitrogen with the liberation of heat occurred primarily at the lead specks and thus offered an explanation for the well known autocatalytic behavior of lead azide in thermal decomposition, the lead specks being the autocatalytic species.

A similar study was carried out for the induction period in the thermal decomposition of lead azide, which is the interval between the commencement of decomposition and the onset of the autocatalytic

stage. Here it was learned that surface compounds form which suppress lead speck growth. These surface compounds were concluded to be primarily forms of basic lead azide produced by the reaction of lead azide with water vapor adsorbed on the lead azide. Lead specks already in existence also could combine with the water vapor to form lead oxide. The autocatalytic stage of the reaction apparently took over after all the adsorbed water vapor had been used up, and the lead specks began to grow.

A technique was developed for producing extremely thin films and microcrystals of lead azide which could be viewed directly by electron transmission with an electron microscope in a manner analogous to the optical microscope. Consequently, replicating procedures were not required with these films and crystals, and continuing observations could be carried out on the same crystal charting the growth of lead specks as decomposition proceeded. Some experiments utilizing microcrystalline techniques were outlined, although it is doubted that at present the utility of the technique is fully appreciated.

Results have pointed out that both anionic and cationic impurities may be taken into the lead azide and influence the sensitivity. The most pronounced effects in this regard were obtained with the strontium cation and the chloride anion. Of more importance, however, is the fact that lead azide appears to be influenced to such an extent by its environment. It is particularly reactive with water vapor and carbon dioxide both of which are generally a part of its normal storage environment. Studies showed that even at ambient temperatures measurable amounts of reaction with these species occurred. The carbon dioxide, however, does not appear to react directly with lead azide. The first step was found to be a reaction with water vapor to form a basic lead azide and hydrozoic acid vapor. Possibly also in the presence of excessive moisture the reaction may continue to lead hydroxide. Carbon dioxide then reacts with the lead oxide portion of the basic lead azide yielding lead carbonate, or if lead hydroxide is present the carbon dioxide may also react with it to form lead carbonate.

The presence of surface carbonates was detected by electron microscopy and infrared spectroscopy, the former being the more sensitive method. The sensitivity of lead azide appeared to be affected by the presence of surface carbonates more than could be accounted for by a simple diluent effect of the inert. This may have been due to an inhibition of lead speck growth on the lead azide surfaces. In the presence of sufficient water vapor lead nuclei would be expected to oxidize and then to react with carbon dioxide to form lead carbonate. An as yet unexplained phenomenon associated with the reaction of lead azide with carbon dioxide is that a gradual recovery of sensitivity appeared to occur.

As shown by photoconductivity measurements, in some instances rather than chemical reactions occurring between the lead azide and its environment, the main effect appeared to be a change in the concentration of "active centers" in the lead azide. Treatments which fell into this category were long term storage at ambient temperature and pressure conditions under nitrogen, dry air, oxygen and argon. Exposure to the first three gases resulted in increased photoconductivity with nitrogen producing the most profound effect. Argon on the other hand as well as storage in a vacuum produced a decrease in photoconductivity. Possible explanations were advanced for these results.

A number of photoconduction bands for lead azide were identified, the most prominent one being at $4060 \text{ \AA}$, which incidentally was the band most greatly influenced by any of the treatments. Hypotheses as to the identities of the active centers producing the various photoconduction bands in lead azide were advanced.

Since the slow decomposition of lead azide occurs by a semiconductor mechanism, i.e., an electron transfer process, one might expect that photoconductivity would be related to lead azide's tendency for "hot spot" formation or sensitivity to initiation. Results of the above study indicate that such a relationship exists, and that photoconductivity is a much more sensitive test than any present tests for sensitivity to initiation. However, before sensitivity and photo-

conductivity can be related one must determine which types of active centers as well as the ranges of their concentrations that are important. Simply an increased photoconductivity does not necessarily mean an increased sensitivity. Storage in nitrogen for example was found to increase the photoconductivity in the 4060 Å band markedly. However no increases in sensitivity were detected. On the other hand, after storage in argon where the photoconductivity rather than increasing continued to drop slightly, the sensitivity also decreased.

Partial decomposition of the lead azide at 250°C of course is a chemical change which is accompanied by the growth of lead nuclei on the lead azide surfaces, and photoconductivity in the 4060 Å showed a corresponding increase. However, when the lead azide was heated in thin layers on flat trays where it could come up to temperature rapidly, the photoconductivity showed a maximum after 10-15 minutes and thereafter decreased. A similar variation in photoconductivity was encountered with a maximum at about the same position when heat treatments were carried out at 150°C. These results showed that effects other than lead speck growth were influencing the photoconductivity as a result of heat treatments. Interestingly samples treated at 250°C (those treated at 150°C were not tested) also exhibited sensitivity maxima in the range 5-20 minutes treatment time in both the light ignition test and the miniature card gap test. This additional active center, which appears to be a larger contributor than the lead specks to the photocurrent in the 4060 Å band, is thought to be of the V_1 type.

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