Formation of explosive compounds in acid-contaminated leaded rubber gloves Part II: Experimental verification

B. Mishra *, A.G. Raraz, D.L. Olson, W.A. Averill

Kroll Institute for Extractive Metallurgy, Colorado School of Mines, Golden, CO 80401, USA

Abstract

   Part I of this paper theoretically analyzed the possible reaction products that can form when leaded rubber gloves are brought in contact with nitric acid. The analysis showed that while the formation of a lead fulminate compound was unlikely, other potentially explosive compounds could form in the acid-contaminated, leaded, rubber glove system. Part II describes the experimental details and the results obtained when the leaded rubber glove samples were reacted with nitric acid. The characterization and some identification of the unstable compound formed by the reaction has been carried out, and its explosive behavior has been measured. The explosive system has two components: the water-insoluble part, which is mainly organic material; and the water-soluble part, which is mainly the lead compound, $Pb(NO_3)_2$. The components are easily separable. These two materials are not explosive individually even after heating. However, in the presence of both the components, an explosion occurs upon heating or upon impact. The explosive behavior of the two component system has been measured. This behavior supports the ideas that these two components interact during the heating period to produce the explosive reaction, and that the oxygen present in lead nitrate is involved in the explosion reaction. It is recommended that a thorough water wash of the nitric-acid-contaminated rubber gloves at room temperature be done to eliminate the explosive system. © 1998 Elsevier Science B.V.

Keywords: Leaded rubber gloves; Explosive compounds; Nitric acid contamination; Flammability; Shock sensitivity

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* Corresponding author. Tel.: +1 303 273 3893; fax: +1 303 384 2189; e-mail: bmishra@mines.edu.

1. Introduction

Part I of this study focused on understanding the chemistry of the leaded, rubber glove/nitric acid system and led to the conclusion that the formation of explosive compounds was probable in that system. It was concluded in part I of this paper that it is highly unlikely to form lead fulminate in this system, particularly in the absence of alcohol. However, several other possibilities were identified, some of which are also explosive in nature. The theoretical approach was also helpful in learning about the safety and health hazards before the development of an experimental work-plan for characterization and identification of the explosive compound.

The compounds that result from the reaction between leaded rubber gloves and nitric acid have been analyzed by X-ray diffraction, IR spectroscopy, and mass spectrometric methods. A colorless lead nitrate with trace amounts of PbO or ZnO has been identified. The explosive yellow material was identified as a mixture of unsaturated organic compounds ($> C=C <$), a nitro-carboxylic compound ($-NO_2$ and $-COOH$), methyl pyridine, dimethyl imidazole, and some organic acids [1–3]. The previous report on the explosive yellow material established that the evolved gases from explosion do not include any amount of lead [1,2]. The detonation products of fulminates usually contain the metallic element, e.g., the explosion products of mercury fulminate include CO, CO_2, N_2, C and Hg [4]. The presence of mercury in the detonation product could be related to its high volatility in comparison with lead.

In the experimental study discussed in Part II, explosive material has been formed by the reaction of Neoprene and Hypalon-lined leaded-rubber gloves and nitric acid. The experimental conditions simulated the reacting system of interest with the exception that there was no plutonium present. Elaborate separation techniques have been employed to collect the different types of products obtained.

2. Experimental procedure

All the experiments were done in an exhaust fume hood with a protective glass door. A thick pyrex protective shield was used between the operator and the chemical reactor. Full personal protective gear was used by the operator to prevent any hazardous incident in the event of an explosion.

2.1. Preparation of glove specimens

Glove specimens were cut from new gloves. The gloves were identical to those used in the glove-boxes at the rocky flats environmental technology site. The gloves consist of a layer of Neoprene-red lead mix sandwiched between two layers of Hypalon. Three square pieces of 15 cm (6 in.) side were used, as shown in Fig. 1. The thickness of different layers of rubber in the glove is reported in Table 1.

To obtain the probable explosive reaction products from experiments where gloves specimens had to be contacted with nitric acid, it was decided to soak the glove specimens completely by immersing the pieces in nitric acid solutions. If any explosive
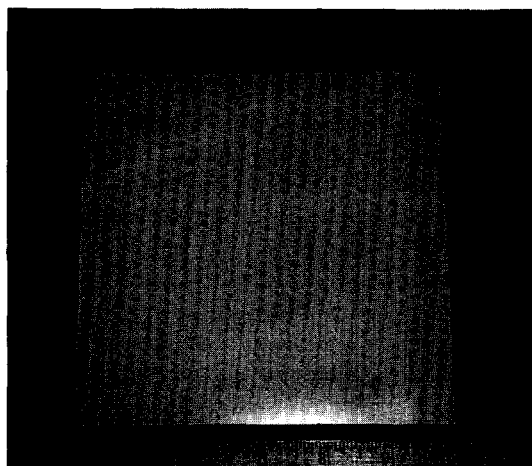
Fig. 1. Glove specimen used in this study.

formed, it would stay in a pool of liquid and would not be generated as a dry product. To compare the influence of nitric acid concentration and temperature on the reactive system, the following experiments were carried out: (1) Room temperature (22°C) exposure experiments in 7 M nitric acid solution for 1440 h (8 weeks); (2) Room temperature (22°C) exposure experiments in 12 M nitric acid solution for 1440 h (8 weeks); (3) Hot acid (50°C) exposure experiments in 7 M nitric acid solution for 96 h (4 days).

Experiments 1 and 2 compare the effect of acid concentration to determine if the explosive formation is a function of the strength of the acid. Experiments 1 and 3 compare the temperature effect to determine if the kinetics of product formation can be enhanced. The two room temperature experiments were carried out in Erlenmeyer flasks with caps to prevent excessive acid evaporation. However, the hot acid experiment required an Erlenmeyer flask with condenser column to maintain constant volume of nitric acid solution and to minimize contamination by NO_2. A hot plate was used for the hot acid experiment 3 and the temperature was controlled by placing a thermocouple in the solution.

The nitric acid solutions were prepared by mixing concentrated nitric acid (15.4 M) with appropriate quantities of distilled water. After the preparation of solutions in the flasks, one piece of glove specimen was introduced in each flask. The experimental steps followed at the conclusion of each experiment and during the analysis of the reaction products were the following.

Table 1
Thickness of glove specimens

Thickness	Outer layer	Central layer	Inner layer	Total
mm	0.756	0.427	0.224	1.41

2.1.1. [A] Solid–liquid separation by filtration

There were two types of solid materials left behind following the termination of the reactions after eight weeks.

(1) The yellow product that resulted from the reaction between the central sandwiched layer of leaded-Neoprene and nitric acid, and which formed as pieces of irregular-shaped brittle material in different sizes. The liquid component of the system was the yellow aqueous acidic solution with acid-soluble reaction product(s), in contrast to a colorless pure nitric acid solution. The solid yellow material was easily separated from the acid solution by filtration.

(2) The two outer Hypalon layers which, after the reaction time of eight weeks, showed virtually no reaction or degradation, and thus were physically separated by pulling out of the solution. It is possible that the adhesive used to put the rubber layers together dissolved in the acid facilitating easy separation of Hypalon layers. Since the middle layer had reacted and the stretched Hypalon rubber layers lost the tension, the two outer layers were crimped.

2.1.2. [B] Liquid disposal

The filtrate was labelled and placed in a disposal container after the chemical analysis.

2.1.3. [C] Solid outer Hypalon layers

The Hypalon layers were washed with water, dried in air, and finally placed in a disposal container in water. The rinse water from this step was considered as part of the filtrate from the reaction products, as indicated in step [A]. The main yellow product that was formed by the leaded-Neoprene and acid reaction and was filtered in step [A] was not washed, since there could be water-soluble components. Instead, this material was dried in air at room temperature within the hood and stored.

2.1.4. [D] Explosion test on the solid yellow product

The dried, solid, yellow product material was first tested for any explosive or combustion reaction on a hot plate. For the explosion experiments, very small (~ 1 g) amounts of material was used. The material was placed in a porcelain crucible and a thermocouple was placed adjacent to the sample. The temperature was raised at a rate of approximately $1°C/s$. The sequence of events was video-recorded and the temperature of explosion was monitored. The reproducibility of the explosion reaction was checked by repeating the experiment several times. A drop-weight test was performed to determine the shock-sensitivity of the explosive material under impact forces. The reproducibility of the data was verified.

2.1.5. [E] Product separation

To prepare the solid yellow product for the analysis, a water dissolution and filtration step was done to separate any water-soluble component(s) from any water-insoluble compound(s). The yellow product material was soaked in water for two days and filtered. The filtrate was dried at room temperature to obtain the crystals of the water-soluble compound. The water-insoluble material was washed and dried at room

temperature. The crystallized water-soluble component was a colorless crystal whereas the water-insoluble component formed a yellow powder after drying.

2.1.6. [F] Explosion test on water-separated products

The dried crystals from the water-soluble fraction and the dried insoluble fraction were separately tested for any possible explosion reaction using the procedure described in step [D].

2.1.7. [G] Chemical analysis

Both the water-soluble and the water-insoluble fractions were analyzed using X-ray diffraction and SEM-EDS methods.

2.1.8. [H] Analysis of the liquid

A small volume of the filtrate from step [A] was taken and crystallized at room temperature within the hood. This product was also subjected first to the explosion test and then analyzed chemically.

2.1.9. [I] Sample storage

It was very important to keep all the materials at room temperature and the solid disposal materials soaked in water. In this way the possibility of any kind of temperature enhanced explosion or reaction was eliminated.

2.1.10. [J] Analysis and testing methods

Identification of compounds using standard analytical techniques was performed. In addition, the behavior of the solid, yellow product under heat and impact force was also tested. The following techniques were used to identify the components and properties of the explosive solid, yellow product: (i) Scanning electron microscopy to gather information on structure and composition of the materials; (ii) X-ray diffraction to identify phases of the solid materials in the system; (iii) Infrared spectroscopy to identify organic materials.

3. Results and discussion

On the basis of EDS-SEM chemical analysis of the three layers, it was possible to distinguish the outer and inner layers of the specimens as Hypalon. Hypalon is distinguished by having sulfur and chlorine in its structure. On the other hand, the middle layer was found to be Neoprene with Pb_3O_4. Neoprene has only chlorine in its structure. Lead was found in the middle layer. Normally, the middle layer is red in color and the outer layers are white. Table 2 partially lists the chemical constituents of the three layers. Other unidentified organic materials are also present in these rubbers. It is important to note that the Hypalon layers have several inorganic fillers. During a test of the glove specimen in acetic acid, two thin layers of some kind of adhesive on both sides of the leaded-neoprene was observed. Fig. 2 shows the three layers of the glove specimen, the color of the layers in this picture is a function of the spectrum developed by heavy elements.

Table 2
Chemical composition of the three layers of glove specimen, as determined by SEM-EDS

Element (wt.%)	Inside layer	Center layer	Outer layer
Si	23.92	–	5.85
S	4.51	–	3.63
Cl	28.05	19.25	60.83
Ti	19.69	–	20.50
Pb	5.89	80.53	4.60
Zn	–	–	–
Al	17.94	0.22	4.59
Mg	–	–	0.61

Three types of material resulted from the glove-nitric acid reaction system, as mentioned earlier: (1) the main product or explosive mixture, which is a pale-yellow, porous, and amorphous brittle material; (2) unreacted Hypalon layers; and (3) the yellow acidic solution. The explosive material was obtained in all the three experiments. There was no significant amount of the yellow, explosive material generated in experiment 1. Very tiny amounts of the yellow material were found mainly on the edges of the test specimen. Neither the water-soluble nor the water-insoluble components from experiment 1 were analyzed further because of the small quantity involved. The lower concentration (7 M) accompanied with a relatively low temperature provided extremely low kinetics of reaction. Experiment 3, which used the same low concentration but at an elevated temperature of 5°C, had rapid kinetics and the product was formed in only 48 h. The experiment was terminated after four days. Thus, the reaction kinetics at room temperature was found to be dependent on the acid concentration, but the rate of reaction can be significantly enhanced by using a higher temperature. By the same token, it is concluded that a higher temperature in association with a higher acid
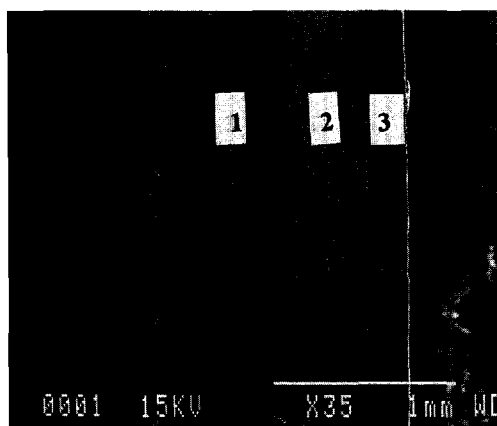

Fig. 2. Photomicrograph of a glove specimen showing its three layers: (1) outer layer, Hypalon; (2) center layer, Neoprene + Pb_3O_4; and (3) inside layer, Hypalon.

Table 3
Observations during the exposure experiments of glove specimens in nitric acid solution

Parameter	Room temperature	Room temperature	Hot temperature
Acid concentration	7 M	12 M	7 M
Temperature (°C)	22	22	50
Reaction time	8 weeks	8 weeks	2 days
Observations during the reaction	Slow decomposition of Pb_3O_4. No formation of brown gases (NO_2). Colorless solution at the end.	Fast decomposition of Pb_3O_4. NO_2 formation. Bubbles on the surface of the center layer. Complete separation after reaction.	Faster decomposition of Pb_3O_4. NO_2 fumes. More bubbles on the reactive surface. Reaction is mainly in the soaked region of the sample.
Appearance of the main product	There is some product on the edges of the specimen.	Yellow main product is porous. The increase in thickness with respect to the new glove sample is about sixfold. The Hypalon–Neoprene interface is rough but the Hypalon–acid interface is smooth.	Yellow main product is less porous. Increase in the thickness of the rubber layers is fourfold. The Hypalon–Neoprene interface is rough but the Hypalon–acid interface is smooth.

concentration would react extremely rapidly. This condition was not tested due to safety concerns.

The major aspects of each experiment are summarized in Table 3. Figs. 3–5 show the photomicrographs of the glove specimen during the experiments as a function of time. The formation of the yellow material and the changes in the physical appearance of the gloves is clearly visible.
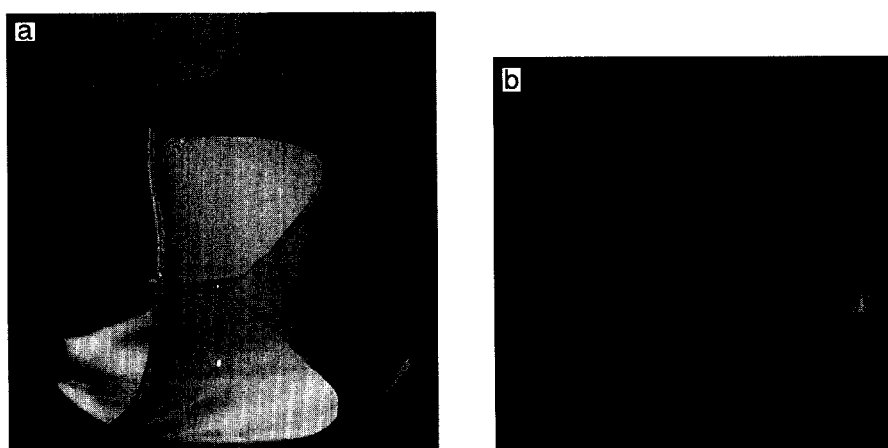

Fig. 3. Leaded rubber gloves–nitric acid reaction system: (A) 7 M acid concentration at 22°C after 8 weeks of exposure shows some reaction at the edges. Solution is clear and is not fuming; (B) appearance of glove specimen after the reaction.
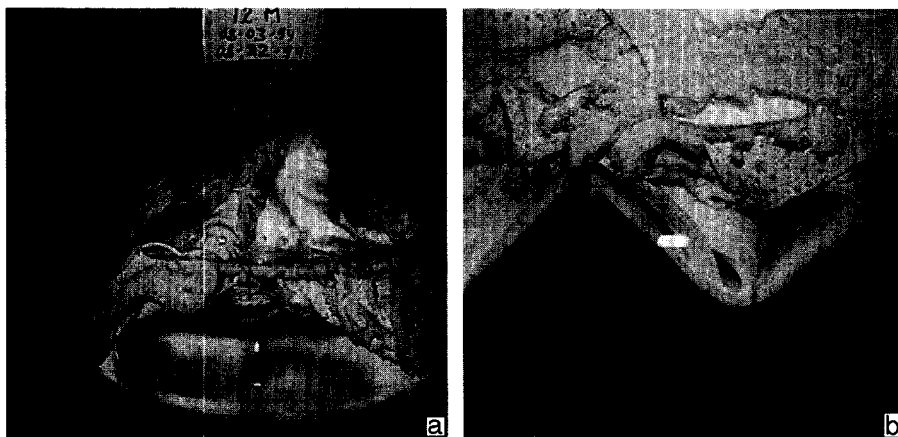
Fig. 4. Leaded rubber gloves–nitric acid reaction system: (A) 12 M acid concentration at 22°C after 2 weeks of exposure shows vapor condensation on the flask wall and brown fumes. Separation of the three layers is almost complete; (B) the separation of the layers and formation of the unstable compound are shown in detail.

A visual inspection of the behavior of solid, yellow product material samples during heating, and the temperature measurement of explosion reaction shows an explosive temperature point of approximately 185°C (± 5). It was observed that this temperature is a function of the nitric acid content in the sample. The important stages during the heating of samples are the melting, white fume formation and the change in color.
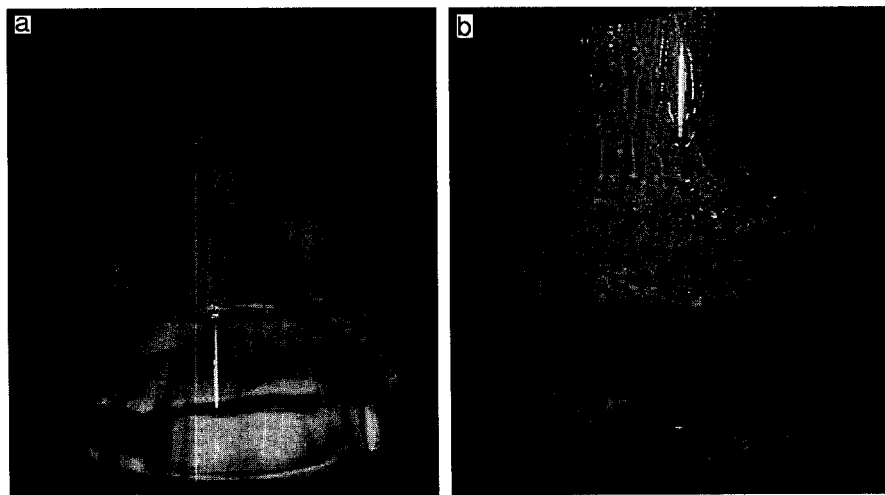

Fig. 5. Leaded rubber gloves–nitric acid reaction system: (A) 12 M acid concentration at 50°C after 2 days of exposure shows higher vapor condensation on the flask wall and brown fumes compared with the low temperature reaction. The reaction is primarily occurring in the soaked part of the glove specimen; (B) separation of the layers and formation of the reaction product is evident.

Having verified the explosive reaction of the solid, yellow product material formed in experiments 2 and 3, a sample from the explosive material from each of those experiments was subjected to a separation process, as described earlier. The goal was to determine if there was a water-soluble portion and a water-insoluble portion in the yellow, solid material. Heating samples of the water-soluble (after crystallization) and water-insoluble compounds separately did not show any explosion reaction. However, after mixing the powder of both the water-soluble and water-insoluble materials back together, an explosion reaction, similar to the one observed before separation of the solid, yellow product material, was observed. Further details of the behavior of the three materials are given in Table 4. Figs. 6 and 7 show the photographs of these materials after heating up to about 300°C. The solid, yellow product is the only material that shows an explosive behavior. The water separated materials melt but do not show an explosive or inflammation reaction. Thus, it can be concluded that the reaction of leaded-rubber gloves with nitric acid produces an explosive system that has two chemical components, neither of which is explosive by itself. Both the components must be present for the explosion reaction to occur. Only one of them is water-soluble.

A sample of the yellow acid solution was also dried until crystallization and the resultant dark yellow material did not show any explosive reaction upon heating. It behaves like the water-insoluble material that melts first, exhales fumes and then becomes an amorphous black material.

The reacted and separated materials were analyzed by XRD, SEM and IR techniques. The XRD pattern of the solid, yellow product material shows some peaks of $Pb(NO_3)_2$. However, the other peaks, which include one with higher intensity, correspond to another compound or compounds, which cannot be identified as any of the known compounds through JCPDS (Fig. 8A). The XRD patterns of the water-soluble components from experiments 2 and 3 are identical and primarily show $Pb(NO_3)_2$, although there are some other unidentified compounds (Fig. 8B,C). Based on its XRD pattern, the water-insoluble material is an amorphous material with some $Pb(NO_3)_2$ peaks in it, as shown in Fig. 8D.

Table 4
Physical and explosive characteristics of the three products

| Parameter	Main Product	Water-insoluble	Water-soluble
Color	Pale yellow	Pale yellow	Colorless
Structure	From room temp. expt.: porous and amorphous. From hot expt. at 50°C: less porous and amorphous	Amorphous with high porosity	Crystals
Behavior during heating	Melts and changes colors from yellow to black. After the appearance of yellow spots an explosive reaction occurs. Formation of fumes.	Melts and changes colors as the main product. There is no explosive reaction Formation of fumes.	Melts. No change in color. No explosive reaction. No fumes.
Temp. of explosive reaction	185°C (average)	–	–
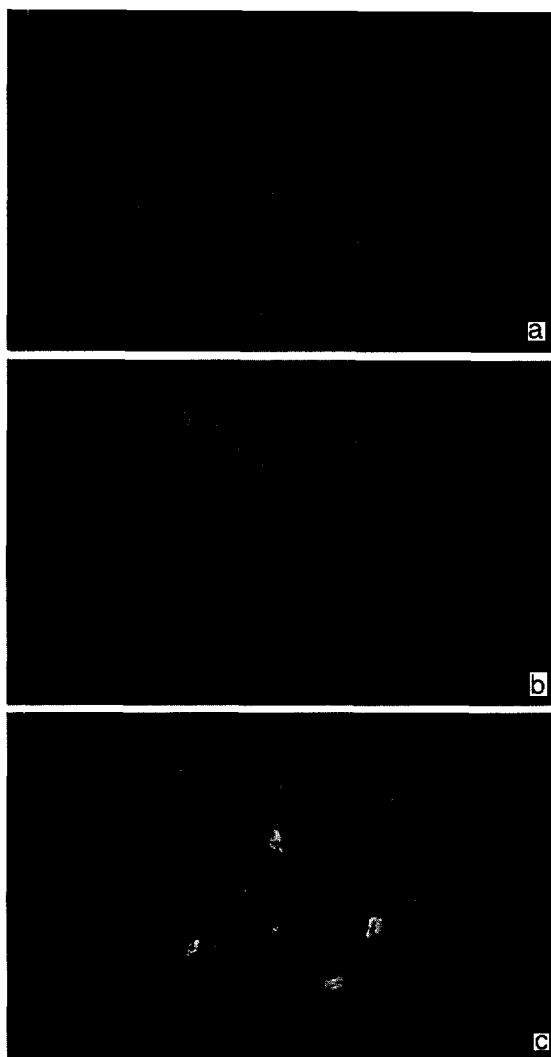
Fig. 6. Photographs of the three products analyzed: (A) reaction product; (B) water insoluble component; and (C) water soluble component.

The EDS-SEM analysis of the solid, yellow product material was not possible to obtain, as the sample was too sensitive and charged. The analyses of the other materials are given in Table 5. It is clear that the insoluble material has primarily lead, sulfur, silicon and high chlorine content, among the inorganic constituents identified by SEM-EDS. As expected, the colorless water-soluble and dark-yellow acid-soluble compounds are mainly lead compounds. The yellow acid-soluble fraction perhaps also contains some organic material.
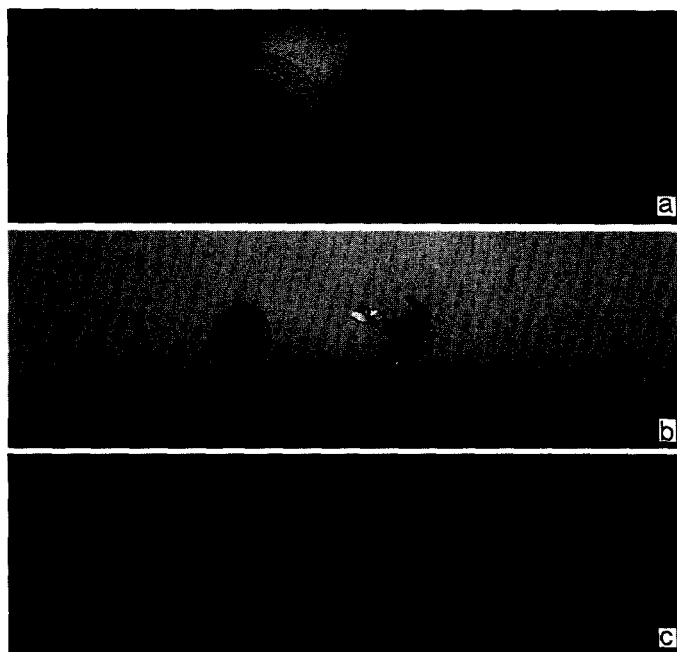
Fig. 7. Physical characteristics of the three products after heating: (A) reaction product after explosion at approx. 185°C; (B) water-insoluble product heated to 300°C; and (C) water-soluble product heated to 300°C.

The infrared spectroscopy (IR) analyses were run to determine the organic constituents present in the solid, yellow product material and its water-insoluble component. As expected, the difference between the IR spectra of the two samples is the presence of lead nitrate in the solid, yellow product material. The wave-number of the fraction of the compound other than lead nitrate, which is present in both the main and water-insoluble materials, has the same magnitude and is different from the values reported for organic lead fulminate (Fig. 9). Lead fulminate is not a possibility in the water-insoluble fraction. The unique band in the solid, yellow product material's spectrum does correspond to a nitrate absorption and thus, supports the XRD data. A search for a possible organic compound with the same wave number was not successful because of the complex composition for organic compounds with closest wave-numbers to the product, as reported in the technical literature.

The melting, fuming and changing of color for the main product during heating but before the explosive reaction suggests that in the process of heating, there may be the formation of some explosive material. The other possibility is that lead nitrate, which is a source of oxygen in pyrotechnics, may induce the explosive reaction. Therefore, the explosive compound, probably, is not the material generated as the main reaction product in this study.

There is no IR information available for the type of elastomers used in this study. This information could provide more insight on the behavior of the glove specimens in nitric acid and the nature of the water-insoluble compound. An interesting observation is
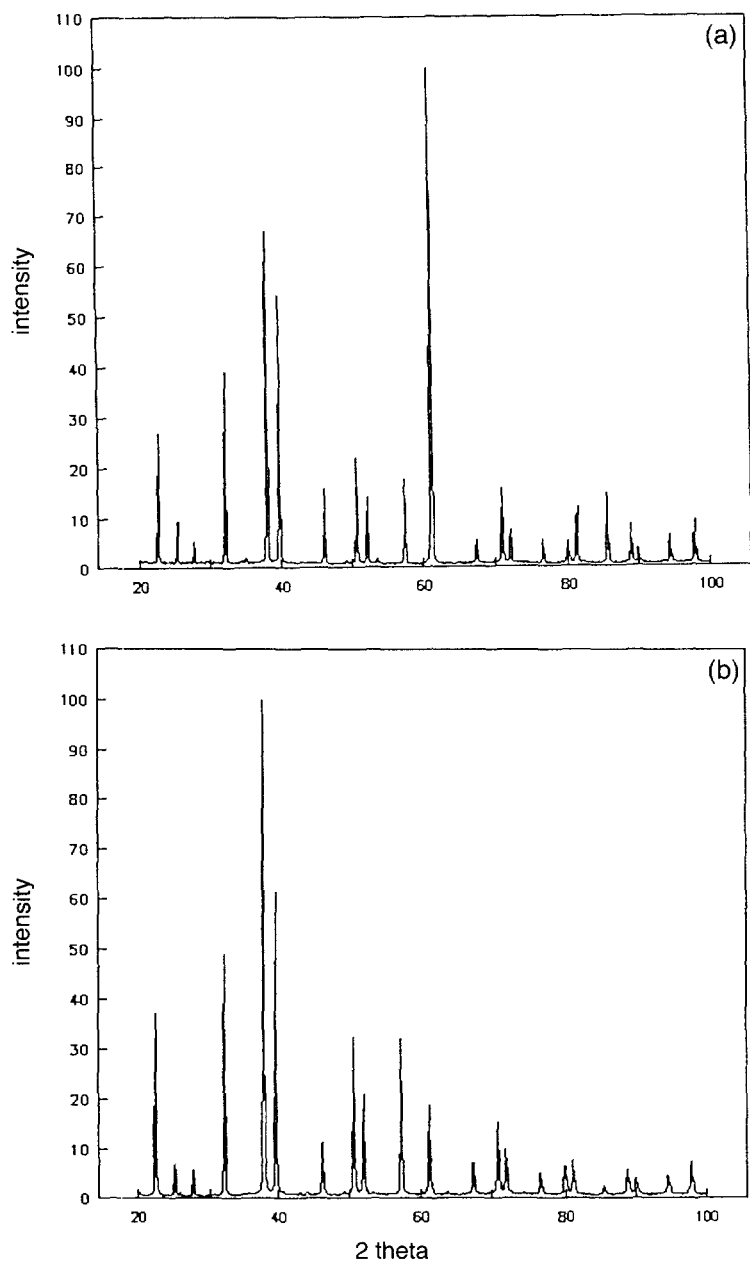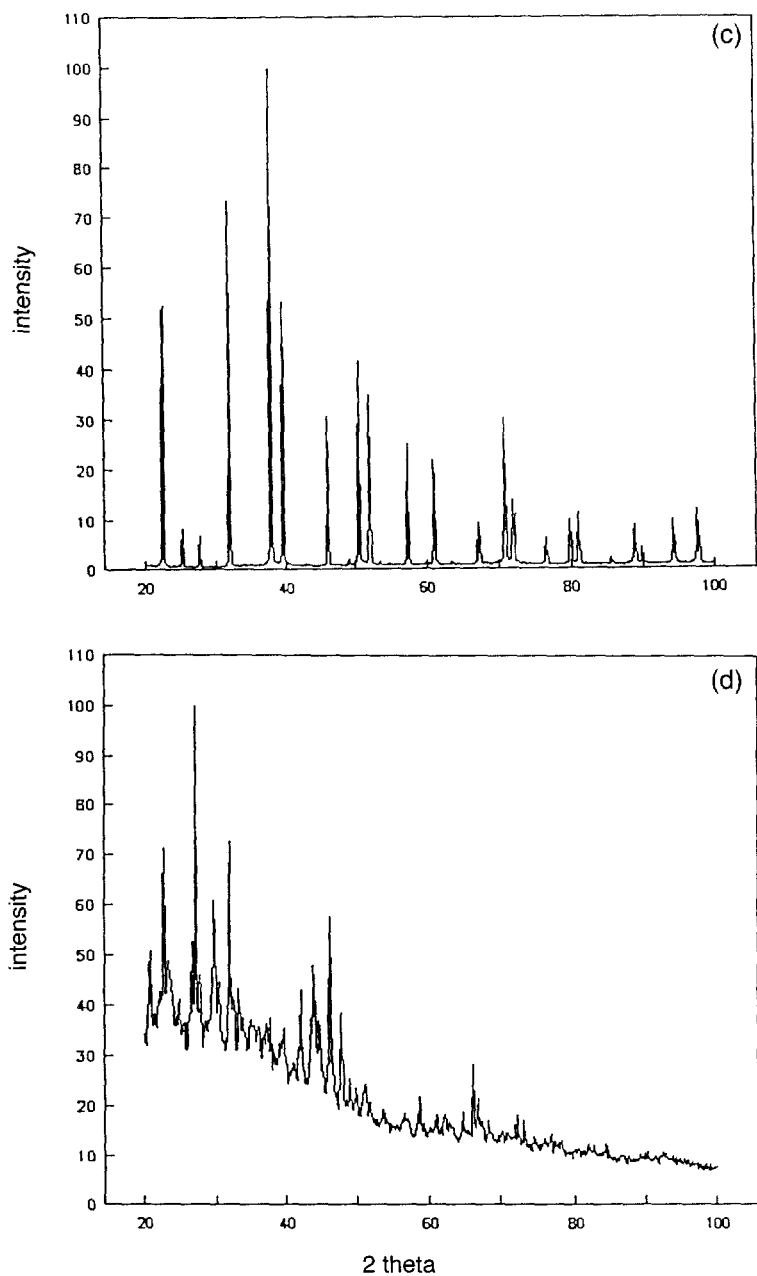
Fig. 8.

Fig. 8. XRD pattern of the three products: (A) reaction product, (B) water-soluble product from experiment 2, (C) water-soluble product from experiment 3 and (D) water-insoluble product.

Table 5
Composition of the products of reaction (wt.%) as analyzed by SEM-EDS

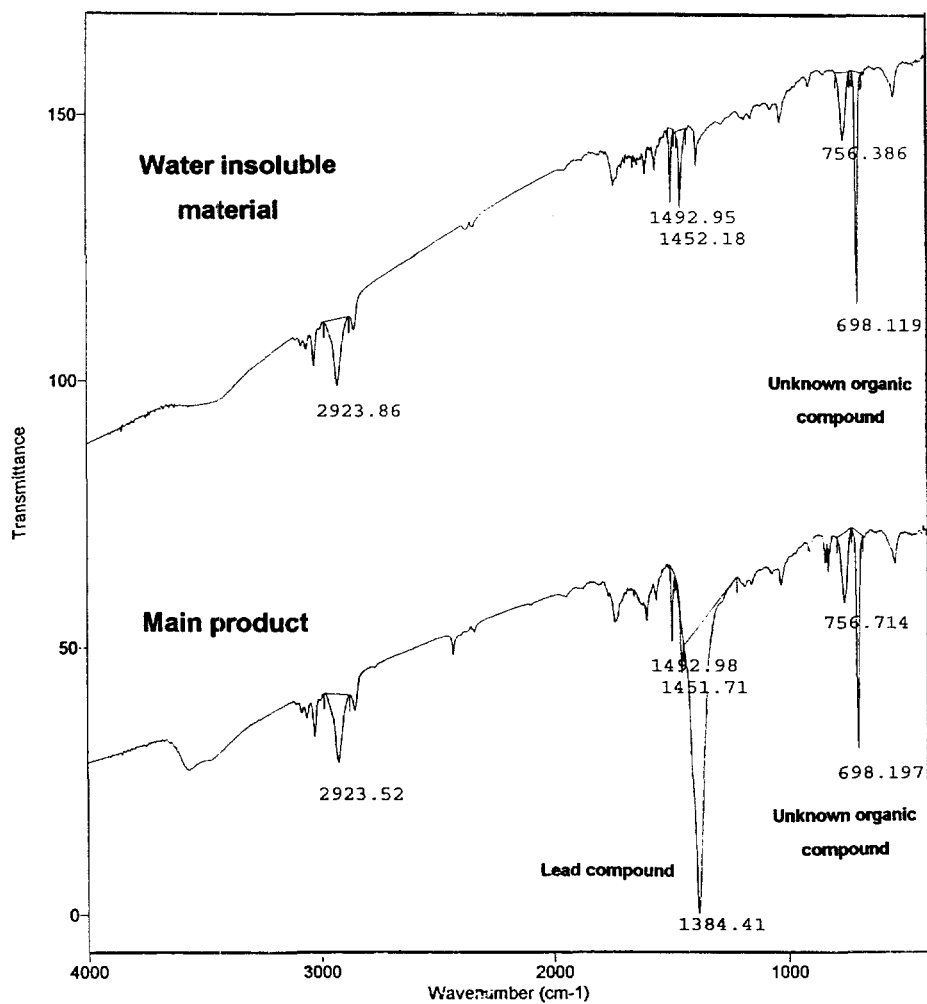| Element	Water-insoluble	Water-soluble	Acid-soluble
Si	7.64	—	—
S	4.55	—	—
Cl	61.27	—	1.38
Ti	—	0.73	—
Pb	26.07	99.27	98.62
Zn	0.46	—	—

Fig. 9. Infrared absorption spectra of the reaction product and the water-insoluble material obtained by FTIR method.

Table 6
Drop-weight test results

Material	Impact force
Main product, an average of 3 mg wt.	180 kg cm[a] or 13 ft lb
Water-insoluble	No sensitivity
Water-soluble	No sensitivity

[a]Reported value: 50–75 kg cm [2].

the presence of sulfur and silicon in the water-insoluble material. Apparently, there is no sulfur or silicon in the original middle layer of Neoprene. Sulfur could have come as a result of the dissolution from the Hypalon layers and silicon might be present in the adhesives.

Based on the XRD and IR analysis it is possible to establish that the explosive compound has two major components: (1) organic and (2) inorganic. The organic compound can be related to the water-insoluble material and the inorganic one to the water-soluble. These two components behave in similar way during heating up to 300°C without an explosive reaction. The reactions during heating of the compound generate a product that has explosive characteristics. There is a possibility that elemental carbon is formed during heating, which in turn reacts with sulfur already present in the system, and perhaps with the lead compound as well (source of oxygen). This explanation is drawn by comparing the behavior of black gun powder, which is mainly carbon, sulfur and some metallic nitrate. The gun powder reacts in a very similar way when heated on a hot plate.

The solid, yellow product material and its water-soluble and water-insoluble components were subjected to the drop-weight test to determine the sensitivity of these materials to impact forces. Only the solid, yellow product material showed any sensitivity to the impact forces. Details of the drop-weight test results are given in Table 6. A clear relationship could not be established between the weight of the sample and the impact force. Possible reasons for this lack of relationship could be the following: (1) different consistency of the samples obtained after room temperature (experiment 2) and high temperature experiments (experiment 3); and (2) influence of the nitric acid content in the samples. There should be a critical mass for a given impact force, which would imply that above this critical mass there is no shock sensitivity. In the drop-weight tests, this critical value for the mass was assigned to the quantity, for which only compression of the sample occurred without any reaction.

4. Conclusions

An explosive compound was obtained as a result of the exposure of leaded-rubber gloves to nitric acid and its physical behavior, explosivity and shock sensitivity were determined using different analytical techniques.

The explosive main product has two components: (a) the water-insoluble fraction, which is mainly organic material; and (b) the water-soluble part, which is mainly lead

compound. The acid-soluble component, when dried, behaves similar to the water-insoluble fraction. These two materials are not explosives separately but undergo an explosive reaction when combined and heated or subjected to an impact. Explosivity is maintained even after the water-separated components are physically recombined. The explosion temperature was determined at 185°C and the material is shock-sensitive at room temperature under a impact load of 13 ft lb.

To obtain more conclusive results and to identify the solid, yellow product material it is recommended to study more rigorously the changes in the chemical composition during the heating period before the explosive reaction.

Acknowledgements

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