Research Article

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Impact and Friction Sensitivities of PETN: II. Sensitivities of the Acidic Material During Manufacturing

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Dedicated to Professor Wolfgang Weigand on the occassion of his 65th birthday

Abstract: In this second part of our work on the sensitivity of pentaerythritol tetranitrate (PETN) the investigations focus on the manufacturing process. Literature about the explosive during production is very rare and optimization or changes in the process demand more in-depth knowledge of the safety parameters. Therefore, the industrial process is imitated in a small-scale laboratory reactor. Then impact and friction sensitivities of emergency drowned, spent acid wet and acid washed PETN are investigated. In advance, PETN samples were taken from the filter of the SSE production and measured in the same manner. It becomes clear at which point a sensitive material is expected in the process. The data will improve handling safety and plant design.

Keywords: PETN · Explosives · Impact Sensitivity · Friction Sensitivity · Testing and Assessment

1 Introduction

The highly energetic nitrate ester of pentaerythritol (PETN) has been successful in various fields for decades. Easy to initiate and moderately sensitive, the compound is suitable in boosters (Pentolite), detonating cords (neat PETN in plastic tubes), detonators (combined with $Pb(N_3)_2$ [1]) or in other formulations (Semtex) [2–3]. Furthermore, PETN is used as a vasodilator to treat angina pectoris [4]. The white crystalline material melts at 141 °C and the decomposition starts at about 20 °C above that [5]. Due to the insolubility in water, it already precipitates during nitration and can be crystallized from many organic solvents [6]. Industrial manufacturing of pentaerythritol tetranitrate goes back to the 1930s [7]. The established methods are often used for good reason. Optimizing or changing the process poses risks and unintentional conversion of material would have disastrous consequences. However, optimization can be useful for economic, safety and environmental aspects. Changes in the supply industry or new legislation can also force changes in the process [9].

Pure common explosives are extensively characterized. In Figure 1 mechanical sensitivities of nine energetic materials are compared. PETN shows to be in the area of a sensitive to very sensitive booster explosive. It is more sensitive than TNT, RDX or TKX-50 but less sensitive than lead azide. In contrast to the pure compounds, much less is known about the properties during manufacturing. To be prepared for future changes or to optimize the existing process, it is necessary to examine the individual manufacturing processes more closely. Here the mechanical sensitivities during the manufacturing of pentaerythritol tetranitrate are investigated further. The production of PETN has developed since the first synthesis in 1894 [10]. Nitration with pure nitric acid followed by filtration, neutralization and recrystallization is now the state-of-the-art process. Pentaerythritol usually contains about 0.8 % dipentaerythritol. Some stability and sensitivity data of crude material is available but a comparison to today's processes is hardly possible. The ICI Explosives Canada investigated two charges of crude PETN to use the acidic product in booster production [11]. The crude PETN (filtrated after nitration) is slightly less thermally stable. The dry materials show similar impact sensitivities to recrystallized PETN. Desensitization through wetting is less

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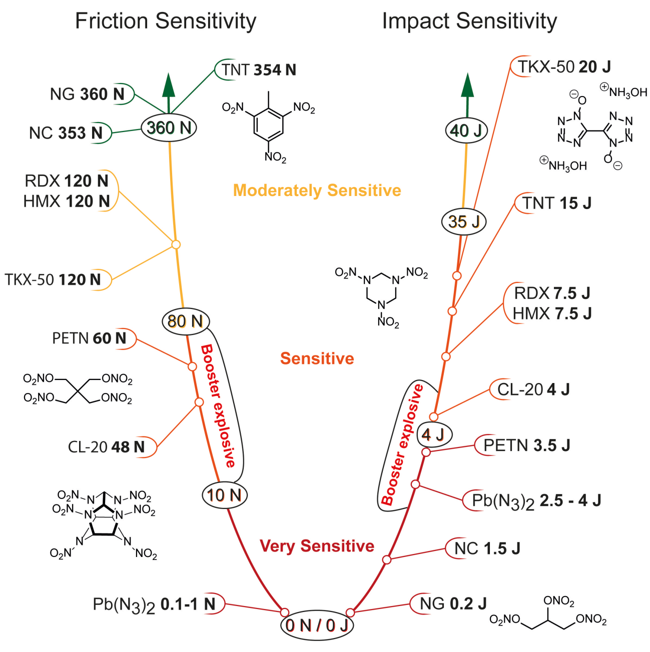


Figure 1. Impact and friction sensitivities of common explosives Trinitrotoluene flakes (TNT), Nitroglycerin (NG), Hexogen (RDX), Octogen (HMX), Dihydroxylammonium-5,5′-bistetrazole-1,1′-dioxide (TKX-50), Pentaerythritol tetranitrate (PETN), Hexanitroisowurtzitan technical (CL-20l), Lead azide ($Pb(N_3)_2$) [5,8].

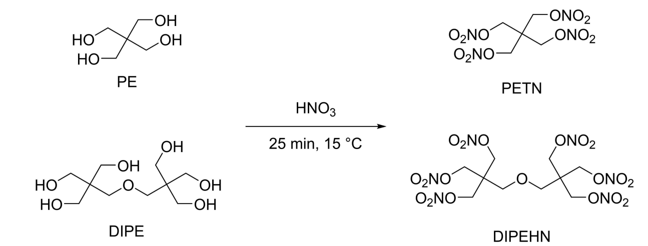
effective for crude material. This indicates differences in the behavior towards mechanical influences.

To better understand the hazards during production the impact and friction sensitivities of emergency drowned, crude acidic and washed PETN are investigated in this work. This should make the existing production safer and prepare for future changes. The sensitivity of water-wet pure PETN is discussed in part one of this series [12]. Some parts of this work are already published at the NTREM [13] and IEC conferences [14] and are shown here for comparison.

2 Experimental Section

Caution: PETN is a highly explosive material, especially sensitive to impact, friction, electrostatic discharge and temperature. When handling, protective measures must be taken depending on the quantity. The reactor setup and procedures were developed as safely as possible, in coordination with BIAZZI and Austin Powder. A solidly grounded reactor with a PTFE stirrer is recommended. Screw fittings and other sources of friction should be avoided or adequately lubricated with silicone grease. Manipulation of the PETN should be done only with soft materials, preferably wet. Wearing Kevlar gloves, wrist and hearing protection behind a blast shield during critical manipulation is recommended.

To synthesize pentaerythritol tetranitrate the corresponding alcohol pentaerythritol is nitrated (Scheme 1). In



Scheme 1. The reaction toward industrial PETN.

industrial production nitric acid with a concentration of >99% is used nowadays. The NO_2 content should be low and checked, as it hurts spent acid stability [15]. The pentaerythritol usually has a content of about 0.8% of its mono ether dipentaerythritol. The nitration in this work is carried out based on the BIAZZI continuous process.

In Figure 2 three simulated industrial scenarios are shown. To not risk an uncontrolled reaction in the event of a malfunction in the plant, the reactor content can be drowned (1) in an excess of water. The controlled process begins with the nitration and filtration of the precipitated material. In the case of spent acid wet PETN (2), the properties of the nitrated material in its residual acid, the spent acid, are examined. Filtration of the spent acid PETN is followed by washing with diluted acid. The sensitivities of this washed product (3) are investigated as well.

2.1 Laboratory and Industrial Samples

Pentaerythritol with contents of 0.1, 0.8 and 1.3% DIPE are used for nitration. The nitric acid shows a concentration of >99% and a low NO_2 content (<0.3%). The nitration was performed in a double-jacketed glass reactor with external cooling and mechanical stirring. Further information about the used materials and the setup can be found in the supporting information. Three different types of PETN were produced: drowned PETN, spent acid wet PETN and washed PETN. The goal was to show the consecutive sensitivities

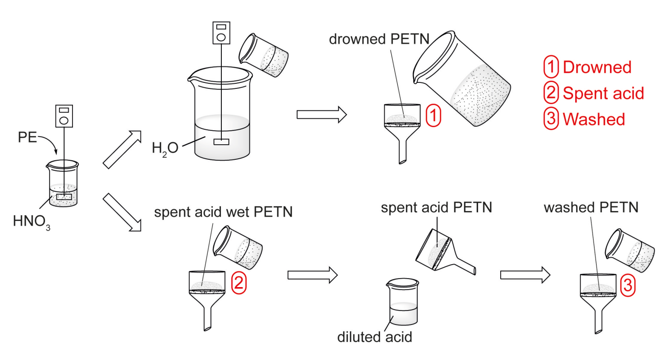


Figure 2. Synthesis of the three different qualities.

from the dry to 35 % wet samples. Therefore, samples were taken from the filter and analyzed for their acid content by either titration or gravimetrically. If necessary the filtrated acid was added to adjust the acid content of the sample. As shown in part I, mixtures of PETN with water tend to be inhomogeneous and lose water during the measurements [12]. It is estimated that the given acid contents vary in the lower percent area.

Synthesis of PETN suspension: A grounded double-jacketed reactor (100 mL) with external cooling and mechanical stirring (500 rpm) was loaded with fuming nitric acid (99.1 %, 50 mL, 75 g, 5 Parts). Pentaerythritol (15.0 g, 110 mmol, 1 Part) containing dipentaerythritol (0.1 or 0.8 or 1.3 %) was added in small portions over 25 min at $15 \pm 3\,^{\circ}C$. A suspension (a) of PETN in 86 % aqueous nitric acid is obtained.

(1) Drowning: The suspension (a) was poured onto water (8-fold amount, 400 mL) which was mechanically stirred (800 rpm). The resulting drowning acid (11.5 %, aqueous nitric acid) was separated from the acidic PETN by suction filtration using a plastic funnel.

(2) Spent Acid: The suspension (a) was cooled to 5 °C and stirred for 30 min. The spent acid was removed by suction filtration over an Omnipore™ 10 μm filter and plastic funnel. On the filter spent acid-wet PETN is obtained.

(3) Washed: The spent acid-wet PETN was dried for 15 min on the filter. Then the crude PETN was transferred into washing acid (150 mL, 11 %, aqueous nitric acid) and mechanically stirred (500 rpm) for 5 min. Suction filtration with a plastic funnel was done to separate the washing acid.

Furthermore, the *"Société Suisse des Explosifs"* was kind enough to provide industrially manufactured PETN samples from their plant. Spent acid wet material was taken directly from the filter after nitration. Then after water-washing and filtration, a second wet sample was taken. This is especially useful to compare laboratory results with industrial production.

In addition, *"Austin Powder Technology"* has provided detonating cord. A cord with 40 g PETN per meter was opened, freed from plastic threads and used for this study.

2.2 Morphology and Particle Size

The dry samples were analyzed by sieving and scanning electron microscopy. The complete data can be found in the supporting information. The data relevant for differentiation are presented in Figure 3.

The samples prepared in the LMU laboratory (0.1–1.3 % DIPE) are comparable in terms of crystal shape and size. Neither the dipentaerythritol content nor the process step has a measurable effect. The PETN is crystalizing in regular blocks that are partly intergrown. The predominant particle size is 100–300 μm with 74 % or more by weight.

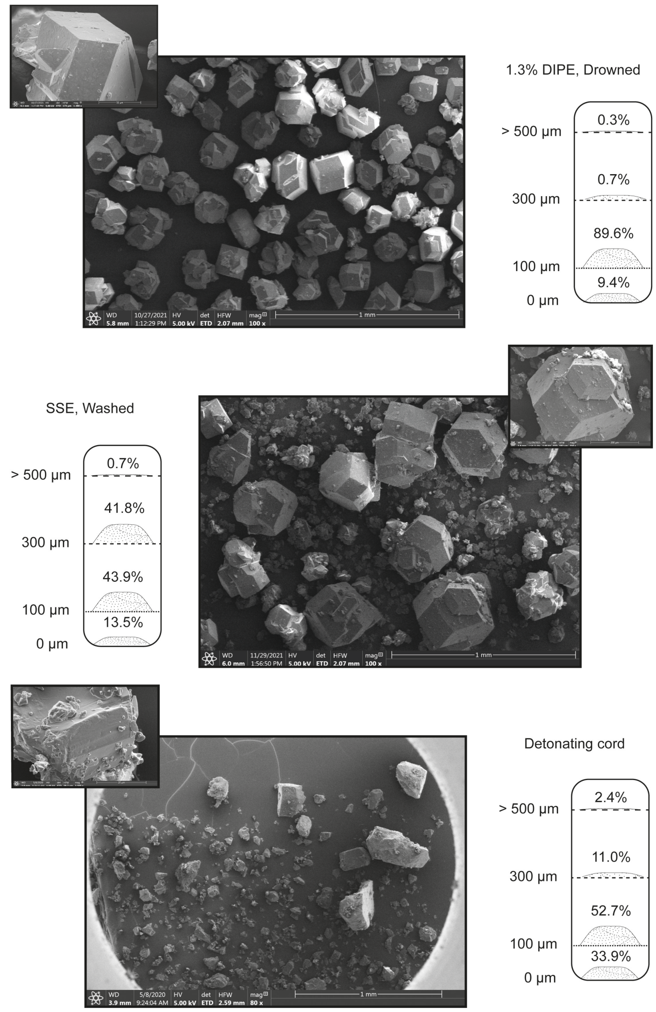


Figure 3. Particle size distribution and scanning electron microscopy pictures of drowned, washed and detonating cord PETN from different sources.

The spent acid wet sample obtained by SSE crystalized as intergrown blocks and agglomerates of smaller crystals. The particles are between 100 and 500 μm with 85 %, thus coarser than the laboratory material. The washed sample shows comparable but smaller crystals in the SEM image. The main particles of detonating cord are 0–300 μm, thus finer than the LMU and SSE samples. On the SEM image, some large fragments are visible that are accompanied by smaller irregular crystals.

Because of manual sieving and electrostatic effects, sieving for smaller particle sizes is less accurate. Furthermore, loosely bound agglomerates and strongly intergrown crystals are hard to distinguish. For future work particle size determination through laser diffraction is recommended. Agglomerates can be broken up by ultrasound and intergrown crystals will stay connected.

3 Mechanical Sensitivities

To better assess the hazards of handling and the safety of the plant, knowledge of the sensitivity of PETN is essential. Mechanical sensitivity measurements are long-established methods to classify the hazards of energetic materials.

Over the years, several methods have been developed, but only a few have gained acceptance. Highly standardized and commonly used are the BAM devices described in the report "Transport of Dangerous Goods. Manual of Tests and Criteria" of the UN [16]. The drop hammer simulates a uniaxial impact on the specimen. This generates heat, shear force and adiabatic compression [17–24]. On the other hand, the friction tester simulates shear forces between roughened porcelain surfaces.

In this way, both devices can simulate a large part of the forces occurring in production. The lower detonation limit is determined with the "one out of six" method. In the following, the results of various samples from the industry and laboratory are compared and conclusions are drawn about the handling of the samples.

3.1 Reference Samples

No comparable or standardized values are available for impact and friction sensitivities during production. Recrystallized PETN from detonating cord and water-wet industrial PETN [25–26] are presented as a reference to better understand the sensitivities obtained. Furthermore, in part I. of our work the sensitivities of wet pure PETN are determined and discussed [12].

In Table 1 the sensitivities of detonating cord and industrial PETN are given. The dry samples show 3–4 J impact and 53–59 N friction sensitivity. The wet samples are desensitized in impact sensitivity to 25 J (9–15 % water). The friction sensitivities for the wet samples vary from 60–80 N (9–15 % water) depending on the institute measuring. The limiting sensitivities for transportation by the United Nations are 2 J and 80 N [16]. The friction sensitivity of PETN is therefore the larger concern.

Table 1. Impact and friction sensitivities of reference samples [25–26] compared with the UN limits for transportation [16].

PETN	Water [%]	IS [J]	FS [N]
Detonating cord[a]	dry	3	56±3
Dried [26]	dry	4	54
Wetted [26]	9	25	60
Wet [25]	9	>25	80
As delivered [26]	15	25	72
UN Transportation limit [16]	–	2	80

[a] Measured at LMU.

3.2 After Drowning

In the case of an emergency on a plant, the reactor is usually poured, drowned, into an excess of water. Then cleaning and disposal are necessary. To ensure safe and efficient working, the mechanical sensitivities of the dry and wet material must be known. In Figure 4 the measured friction and impact sensitivities of drowned PETN are shown. The colors indicate the different DIPE contents in the starting material.

For the friction sensitivities, a slightly decreasing trend is observed. The wetter the material the lower the sensitivities. The dry material shows to react at around 60 N, which is comparable to pure PETN. The sensitivities then decrease to around 84 N (15 % wet). Until 35 % drowning acid content the sensitivities stay unchanged. The DIPE content does not have a significant influence that can be detected.

The impact energy necessary for detonation is also increasing with higher drowning acid contents. The dry material shows to be around 4 J, like pure PETN. When wetted, an increase above 20 J (10 % wet) is observed. Above 10 % drowning acid, the sensitivities stagnate around 20–25 J.

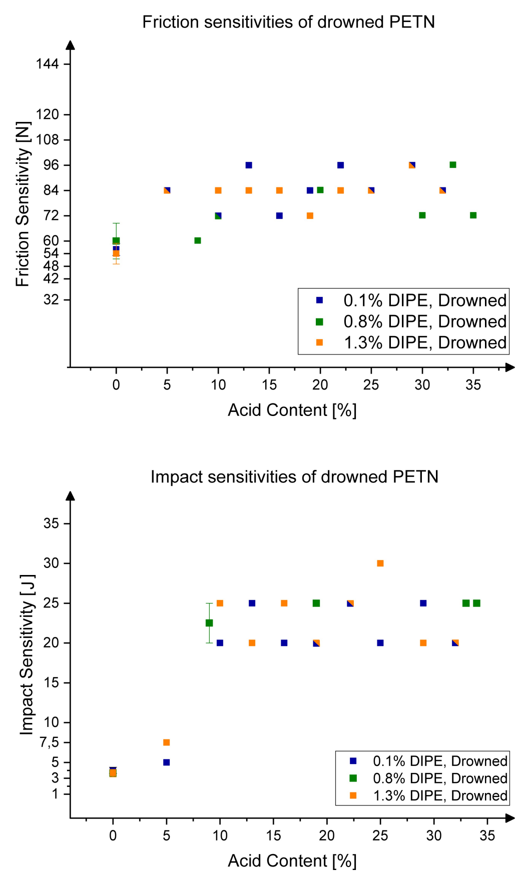


Figure 4. Friction and impact sensitivities of drowned samples containing drowning acid in amounts of 0–35 %.

3.3 After Nitration

In today's PETN nitration process, the product is precipitated directly from the nitric acid. Through the reaction the acid is diluted to around 85 % concentration, then called spent acid. The crystallization causes acid to be occluded within the crystal. These suspensions are mechanically stressed by pumping and filtration. In Figure 5 the friction and impact sensitivities of the spent acid wet and dry material are given. Furthermore, the LMU samples are compared with the industrial SSE PETN after nitration. The LMU samples and SSE samples are in line with the trend and are comparable.

Unexpectedly, increased friction sensitivities are observed for many spent acid-wet samples. The dry materials show sensitivities around 60 N. When wetted, the sensitivities mostly stagnate between 48 and 72 N. The 1.3 % DIPE sample was measured with only 36 N at 16 % acid content. This increase in sensitivity was not observed in any other form or mixture of PETN.

The impact sensitivities, in contrast, show a decreasing trend. With around 4 J the dry material is comparable to pure PETN. The decrease slowly takes place when wetting up to 15 % acid. In this area of decrease, the deviations are rather high and no concrete statement can be made. Between 15–35 % acid the impact sensitivities are around 15–20 J.

3.4 After Nitration and Washing

After the nitration and filtration, the crude PETN is washed with diluted nitric acid (11 %). This suspension is then stressed through vigorous stirring, filtration and pumping. The mechanical sensitivities of the washed samples are represented in Figure 6 and compared with the washed sample taken from the SSE production.

The friction sensitivities are slightly decreasing when more washing acid is present. This trend can also be observed for the SSE sample. The dry samples show sensitivities around 54 N, similar to pure PETN. The addition of acid causes the sensitivities to slightly decrease up to around 84 N (20 % wet). The SSE samples show to be slightly more sensitive than the LMU samples but the deviations, in general, are rather high. For the SSE and the 1.3 % DIPE sample a sensitivity of 60 N is observed at 29 % wet. A general decrease is detected but some exceptions are present and caution is advised.

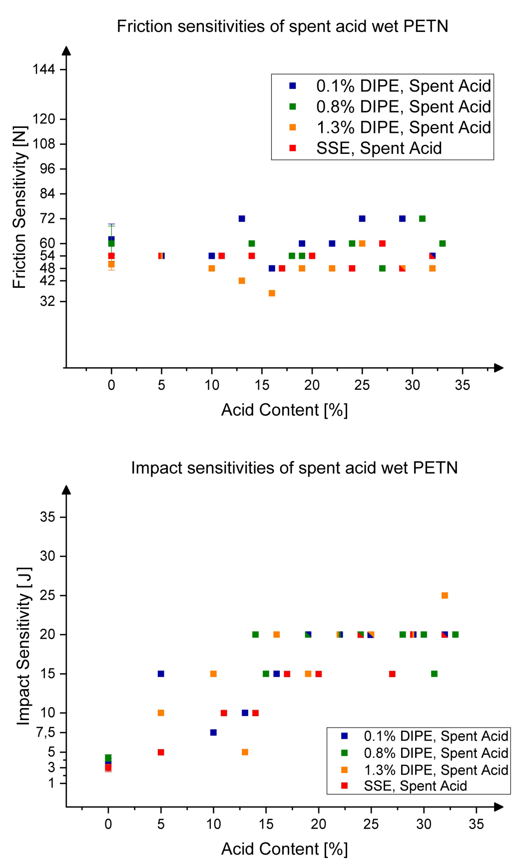


Figure 5. Friction and impact sensitivities of PETN after nitration containing spent acid in amounts of 0–35 %.

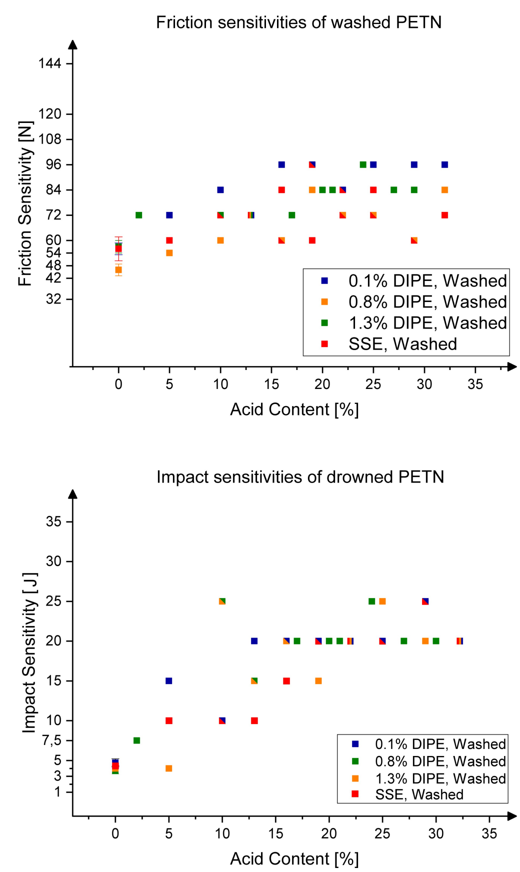


Figure 6. Friction and impact sensitivities of washed PETN containing washing acid in amounts of 0–35 %.

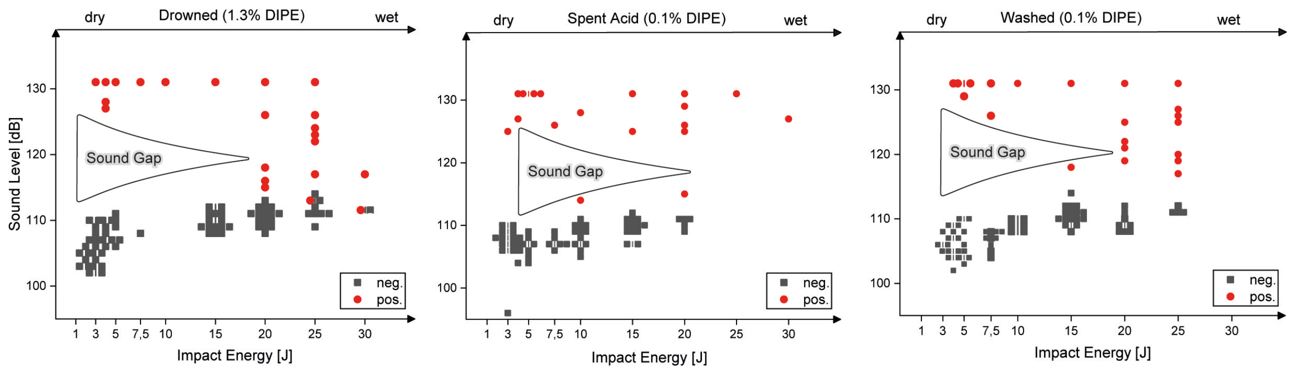


Figure 7. Sound level of impact sensitivity tests at different DIPE contents and drop energies. Red dots are evaluated by the operator as positive results, grey squares are negative results.

The impact sensitivities again show a different trend. A strong decrease with rising acid content is observed. The dry material is tested to be around 4 J. When washing acid is added desensitization takes place. Above 16 % acid content the sensitivities stagnate at 15–20 J. The area of decrease again shows large deviations and is of high uncertainty. Above 15 % acid the sensitivities are 20–25 J. The SSE samples show a comparable trend with the LMU samples.

3.5 Sound Level of Impact Sensitivities

After the first few impact measurements, it was audible that the detonations of the wet samples are less violent. Often residues of unreacted material were found in those test sleeves. To record this information, the noise level was detected in dB using a microphone about 30 cm away. Any kind of detonation was counted as a positive result regardless of how loud it was. In Figure 7 the sound levels of the drop experiments are shown. Positive results, detonations, are marked in red and negative results in grey. The negative results tend to stay between 100–115 dB. This noise is generated by the impact of the weight and increases with the mass of the weight. The explosions of the dry materials are in the area of 130 dB (maximum measurable value). The operator can evaluate the result using the microphone alone. When the samples are wet and incomplete conversion happens the noise of the detonation is decreasing. This can happen up to a point where the detonation is quieter than the basic noise of the machine. The operator can clearly distinguish the detonation and background but the microphone does not. For the acoustic evaluation of TNT impact tests, similar problems are observed by Marrs et al. [27].

The drowned and washed samples both show a strong decrease in noise when the conversion of the material is incomplete. Nevertheless, there are wet samples that show full conversion accompanied by a violent sound. The spent acid wet samples are generally more violent and show less incomplete conversion. The incomplete conversion means that the sample initiates but the detonation does not propagate. The diluted acid does inhibit detonation propagation. However, initiation of PETN in spent acid, showed to propagate more easily.

4 Conclusion

The goal of this work was to outline the differences between PETN during manufacturing and the known final product. Therefore, PETN was synthesized from PE with 0.1 to 1.3 % DIPE. The mechanical sensitivities were investigated after emergency drowning, during nitration, and after washing the crude product. No dry sample was found more sensitive than industrial PETN. Altering the DIPE content did not change the sensitivities significantly. The drowned and the washed samples are acting very similarly towards wetting. Both are desensitized by higher liquid contents whereas the effect is much more dominant for the impact sensitivities. The effect appears to be linear at least up to 25 % liquid content. For the PETN during nitration, a drastic difference is observed. The wet material showed to be more friction sensitive than industrial PETN. The impact sensitivities are decreased when the material is wet.

It can be concluded that spent acid wet PETN represents the greatest hazard in the process. Drowning or washing leads to a product that is comparable sensitive to the final product. In general, friction sensitivities show to be the greater concern. Soft materials and careful manipulation are recommended.

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Data Availability Statement

Data may be requested via the authors.

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