

## Effects of crystal habit modifiers on characterization parameters of tetrazene

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*This work has studied the effects of modifying agents on the behavior of industrially important primary explosive – tetrazene. Namely, of interest were the powder characteristics (particle size, bulk density and angle of repose) and sensitivities to external stimuli (friction, impact). The agents consisted of a wide group of materials when the following ten were selected: dextrin, sodium carboxymethylcellulose, gum arabic, sodium laurylsulfate, p-toluenesulfonic acid, polystyrenesulfonic acid, 1,6-diaminohexane, polyacrylamide, sunflower lecithin, and bone glue. No general correlation between the agent structure and the results were found, but some partial behavior patterns could be identified. The bulk density ranged from  $0.2 \text{ g}\cdot\text{cm}^{-3}$  at the low end for unmodified samples to  $0.5 \text{ g}\cdot\text{cm}^{-3}$  at the highest improvement. The angle of repose shifted from  $60^\circ$  for the unmodified form to  $52^\circ$  at best flowability (for the ball ammonium perchlorate as a reference value of  $30^\circ$ ). The effect on the friction sensitivity is minuscule and all the samples had their  $F_{50}$  values within 3–7 N range. Three different groups separated for the impact-stimulus behavior – unaffected, sensitivity lowered to that of PETN or RDX, and erratic behavior. The particle size was generally in the  $100 \mu\text{m}$  scale, but the crystal habit varied significantly.*

**Keywords:** Tetrazene; Characterization; Crystal modifiers; Sensitivity; Bulk density; Flowability

### Introduction

Tetrazene is an important primary explosive that, in this year, celebrates a 100-years, since the first patented industrial use of the substance has been reported [1]. This substance has found its main use as a sensitizer in percussion and stab priming

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mixtures [2], such as those found in cartridges and initiation devices of other munitions products, where they ignite the performance charge. In addition, tetrazene at a higher percentage content not typical for sensitizers is used in the NONTOX composition [3] as the main performance ingredient and in compositions for special use [4].

Despite a long history of use, the information known about tetrazene is largely lacking when compared to other successful primary explosives. This is especially true, when considering the effect of crystal habit on industrially significant parameters, such as sensitivity, performance, and powder characteristics. Best comparisons are drawn with lead azide and diazodinitrophenol (DDNP, dinol), where the effects of crystal habit and crystallization modifying agents have been studied extensively. Lead azide is a material with parameters which are significantly affected by modifying agents present during the preparation and DDNP faces the same challenges as tetrazene with respect to the fact they both form in a crystal habit that results in powder of undesirable behavior.

Lead azide forms four allotropic modifications:  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  [5]. Only orthorhombic  $\alpha$  modification is a desired form of the industrially produced lead azide as other forms or mixtures thereof are more sensitive to mechanical stimuli, thus being more hazardous for processing. The formation of  $\alpha$  modification is preferred when certain crystal structure modifiers are introduced during the lead azide precipitation. The most commonly noted include dextrin, polyvinylalcohol, carboxymethylcellulose, and animal glue [5–9]. Particularly the addition of dextrin is known to immensely decrease the impact sensitivity of the resulting lead azide. The products also form more free-flowing particles that are desirable for reliable volumetric measuring and the loading of lead azide into detonators. Use of certain modifiers (e.g. eosin) leads to the formation of monoclinic  $\beta$  modification of lead azide forming long needles [10].

In the case of DDNP, several methods for preparation of free-flowing material were published in the past [11–15]. Two of them are based on using the crystal-structure modifiers. Garfield and Dreher have patented the triphenyl-methane dyes as crystal growth control ingredients that lead to formation of tabular crystals. The optimal amount of these modifiers is 0.5–2 % of the weight of picramate employed [11]. Alexander suggested various phenols, aromatic nitrocompounds and amines for production of free-flowing DDNP [12].

Research on the effect of crystal habit modifiers on the tetrazene behavior is limited and often relegated to patent literature, where the information available tends to be of general nature or focused on the preparation process with little to no quantitation of the effect. Taylor suggests the use of dispersing agents in order to obtain granular material free from acicular and fragmented crystals. He specifies the agent to be of the anionic type at concentrations between 0.02–0.2 % (*w/w*) of the total reacting solutions [16]. Schönbeck and Duguet propose the use of animal proteins, vegetable gums, waxes, colloids and soluble synthetic polymers in concentration of 0.005–1 % of the total reaction weight to obtain compact a well-flowing product [17]. Gidasov et al. achieve the same goal by a special dosing method and the addition of combined aqueous solution of dextrin and gelatin [18].

The study on the crystal habit and morphology is important for industrial application, but for a bulk material with unsuitable characteristics may pose complications during further processing. Among such difficulties, one can consider a poor drying, caking, difficult use in automatic filling machines, tendency to dust, adhesion to surfaces and poor quality of final mixtures [16–18]. Herein, we decided on investigating the effect of a wide group of agents on the behavior of tetrazene with the aim of quantifying the effect on sensitivity and important powder characteristics; both being crucial for industrial application.

## Materials and methods

### Sample preparation

Tetrazene was prepared according to the guidelines in [19]: Stock solutions were prepared by bringing 388.0 g of sodium nitrite to 1000 mL total volume, 241.4 g of aminoguanidine sulfate (AGS) to 1000 mL and 0.65 g of modifying agent to 50 mL total volume. A jacketed reactor fitted with stirrer and thermometer was fed with 20 mL sodium nitrite solution (112 mmol), 11.4 mL solution of the agent and 40 mL AGS solution (39 mmol) in this sequence. The mixture was brought up to 100 mL total volume with water and the reaction mixture was adjusted by the addition of enough 10 wt.% acetic acid to adjust pH of the mixture into the initial value range of 5.6–5.8. This mildly acidified mixture was stirred at 200 rpm., heated to 56–58 °C, and held at this temperature for 35 min. after the precipitation started before cooling the mixture. The solid was filtered off and washed with water and acetone. Additives and any changes in conditions are listed in Table 1 along with relevant results of analysis.

### Instrumentation and analysis

The reaction mixture pH was measured using a pH meter Schott Lab 850 (Schott Instruments, Mainz, Germany) equipped with pH electrode (model BlueLine 14 pH, SI Analytics, Mainz, Germany). A set of buffer solutions with pH 4.00, 7.00, and 10.00 (Fisher Scientific, Pittsburgh, PA, USA) were used for three-point calibration of the indicator electrode.

Differential thermal analysis was carried out with a thermal analyzer (model DTA 550 Ex, OZM Research, Hrochův Týnec, Czech Republic). The samples were tested in open glass micro-test tubes in contact with air. The weight of samples was 3–5 mg, the heating rate set to 5 °C min<sup>-1</sup>. Decomposition of tetrazene was accompanied by a strong acoustic effect and the destruction of the micro-test tube.

**Table 1** Material characterization and powder parameters of tetrazene samples

Sample / Modifier	Yield [g] (theory [%])	C [%] (for theoretical values, see legend)	H [%]	N [%]	$T_d$ [°C]	$\alpha \pm \sigma$ [°] ( $\sigma$ [%])	$\rho_B \pm \sigma$ [g·cm <sup>-3</sup> ] ( $\sigma$ [%])
Needles	5.71 (77.5)	12.91	4.32	74.05	136.3	53.7 ± 2.4 (±4.4)	0.24 ± 0.01 (±5.19)
Unmodified RPM 100	5.56 (75.4)	12.72	4.23	73.93	140.4	59.9 ± 1.8 (±3.0)	0.30 ± 0.01 (±2.79)
Unmodified RPM 200	5.70 (77.4)	12.68	4.20	74.08	138.9	60.0 ± 2.5 (±4.1)	0.25 ± 0.01 (±4.52)
Unmodified RPM 300	5.67 (77.0)	12.91	4.25	74.37	138.4	59.9 ± 0.9 (±1.5)	0.23 ± 0.00 (±2.05)
Re-precipitate	—	12.89	4.23	74.00	132.9	—	—
Dextrin	5.70 (77.3)	13.02	4.13	73.28	139.6	56.0 ± 1.5 (±2.7)	0.42 ± 0.00 (±1.08)
Sodium carboxymethyl- cellulose (NaCMC)	5.40 (73.2)	12.71	4.19	74.16	140.8	55.1 ± 2.2 (±4.0)	0.42 ± 0.01 (±2.10)
Gum arabic (Gum)	5.68 (77.0)	12.92	4.20	73.87	139.2	59.8 ± 1.7 (±2.8)	0.27 ± 0.01 (±2.99)
Sodium laurylsulfate (SLS)	5.64 (76.6)	12.90	4.22	73.71	139.7	57.3 ± 1.0 (±1.7)	0.44 ± 0.01 (±1.26)
Polystyrenesulfonic acid (PSS)	5.63 (76.5)	13.02	4.24	74.02	138.7	56.4 ± 2.2 (±3.9)	0.34 ± 0.01 (±2.36)
Para-toluenesulfonic acid monohydrate (PTSA)	5.67 (77.0)	12.87	4.20	73.92	139.2	62.3 ± 1.2 (±2.0)	0.26 ± 0.01 (±2.46)
1.6-diaminohexane (DAHex)	5.67 (77.0)	12.96	4.23	74.06	139.8	59.6 ± 1.0 (±1.7)	0.29 ± 0.01 (±3.19)
Polyacrylamide (PAM)	5.77 (78.3)	12.83	4.23	74.16	139.5	59.6 ± 1.6 (±2.8)	0.24 ± 0.01 (±3.27)
Sunflower lecithin	5.50 (74.7)	13.12	4.23	73.24	137.3	54.7 ± 0.2 (±0.3)	0.37 ± 0.00 (±0.73)
Bone glue	5.66 (76.9)	13.11	4.25	73.92	139.7	51.7 ± 0.5 (±0.9)	0.48 ± 0.00 (±0.62)

*Legend:* Theoretical values: C [%] = 12.77, H [%] = 4.29, N [%] = 74.44;  $T_d$  [°C] = 135–140 (according to [5]), where:  $T_d$  – temperature of decomposition;  $\alpha$  – angle of repose,  $\rho_B$  – bulk density,  $\sigma$  – standard deviation

Elemental analysis was carried out using automated elemental analyzer (UNICUBE, Elementar, Langensfeld, Germany) when sampling 1–2 mg of tetrazene. This substance was visualized with a scanning electron microscope (SEM; Jeol JSM 5500 LV, JEOL, Akishima, Japan). The bulk density was measured in a small-scale custom block of 5.12 cm<sup>3</sup> in volume. Measurement was repeated five times.

Flowability was measured as the angle of repose which was determined on a small scale by measuring the height of the pile formed after two identical cylinders of 2.5 cm in diameter and sitting on top of another one filled with the material; both being vertically separated [20]. Measurement was made again in five replicates. The angle of repose is calculated from the equation:

$$\alpha = \operatorname{arctg} \frac{2 \cdot \text{pile height}}{\text{cylinder width}} \quad (1)$$

Sensitivity to friction was determined using small BAM apparatus of FSA-12 type. Testing set consisted of porcelain BFST Pt 100 25 × 25 mm plates and BFST Pn 200 pegs. Sensitivity to impact was measured using Kast fall hammer. Testing sets composed of steel guides BFH-SC and cylinders BFH-SR. All the apparatus and related supplies for sensitivity measurement were manufactured by OZM Research. Sensitivities to friction and impact were evaluated using a probit analysis at 15 trials at each intensity level (at least 5 levels where possible) and the results were expressed as a friction force or impact energy with a 50% probability of initiation [21].

## Results and discussion

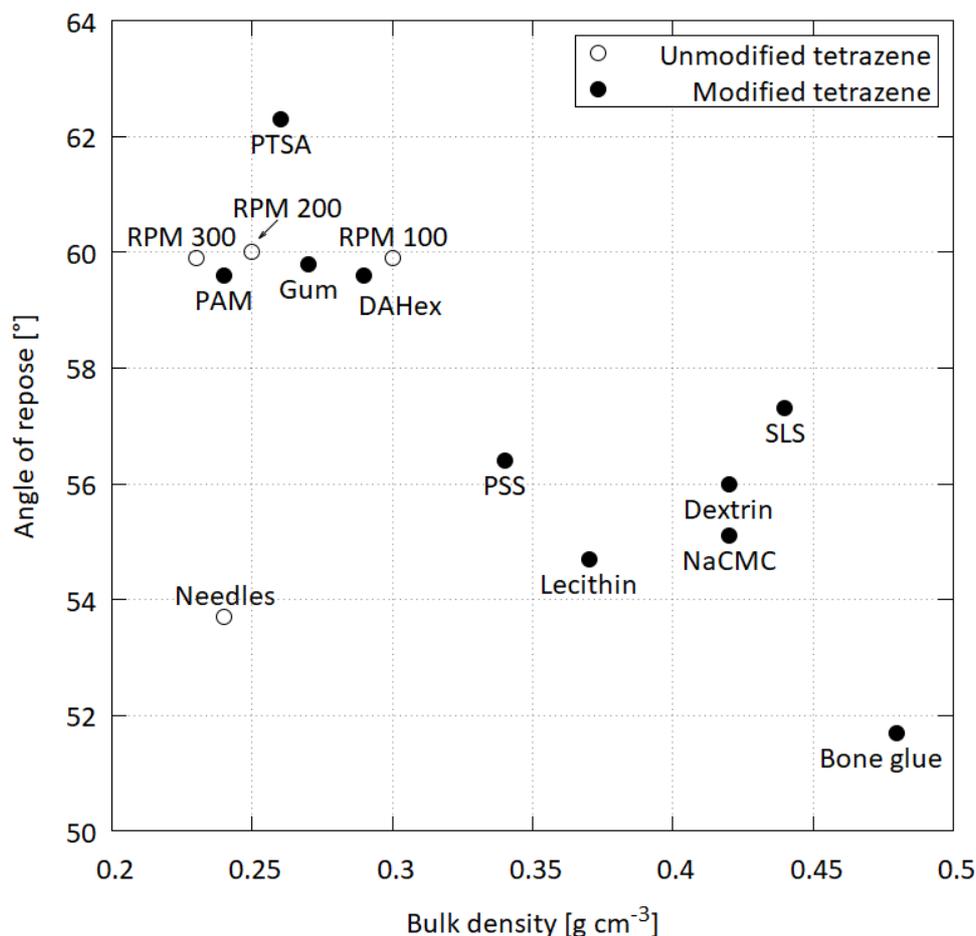
### Particle morphology

The angle of repose and the bulk density are both parameters of importance for characterization of any powder material for industrial application; especially, where automated machines are being employed. Whether a modifier or process change would have an effect on the tetrazene morphology, it is reflected in these characteristics, best observable in a scattergram of the angle of repose vs. the bulk density (see Fig. 1). The more a process changes or a modifier approaches the right bottom corner of this diagram the higher the improvement in the industrial processability. The higher the bulk density the more similar the material compared to other materials in the final mixture, thus improving homogeneity. And oppositely, the lower the angle of repose the higher the flowability of the powder, which simplifies transportation, loading, and general manners of handling by automated machinery.

### *Unmodified form of tetrazene*

Tetrazene is known to give rise to acicular or needle-shaped particles that, in the bulk, form a material of poor quality for the industrial processing [16–18]. This behavior can be observed on all the samples devoid of modifiers prepared by the above-mentioned method, which is similar to industrial procedure.

These needles have a tendency for twinning and fragmenting, resulting in X, Y and dendritic shaped particles. These motifs are then preserved even with the decreasing particle size resulting from the increased turbulence during preparation (higher RPM), as seen in Fig. 2 (RPM 100, RPM 200, RPM 300 and Needles). Re-precipitated sample is not included as it is not representative of the reaction normally used to obtain tetrazene.



**Fig. 1** Comparison of angle of repose to bulk density of tetrazene samples

Regardless of the particle size tetrazene from this process forms a powder material of similar characteristics (Fig. 1). The angle of repose remains at  $60^{\circ}$  and only the bulk density is slightly affected. Ball ammonium perchlorate serves as a reference point for a material of very good to excellent flowability ( $30^{\circ}$ ) as compared to tetrazene, which is a material with poor to very poor flowability.

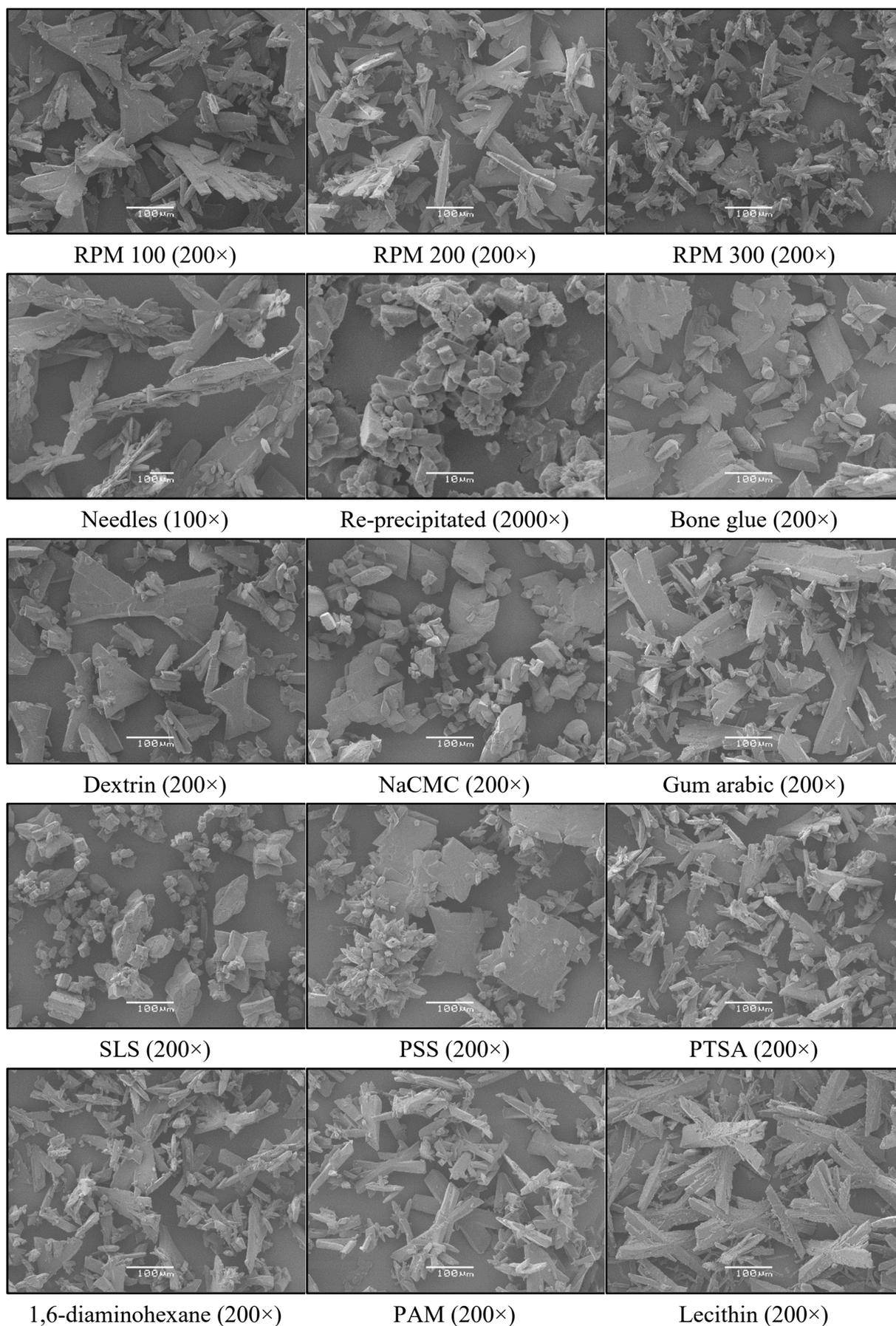
This grouping will form a base area of parameters to which tetrazene modified with additives will be compared. The only outlier of this group is the form of tetrazene needles, where the particle size is so great that the angle of repose is reduced by the sheer momentum of pouring particles.

### *Modified form of tetrazene*

The effect of various modifying agents present during the tetrazene preparation is demonstrated on the diagram in Fig. 1, showing that two distinct groups are formed. First, a group of additives with little to no effect on bulk material behavior – these consist of PAM, PTSA, gum arabic and 1,6-diaminohexane. Indeed, these additives exhibit a little effect on the crystal habit when SEM images (Fig. 2) of the samples are compared with unmodified sample of the same process. In fact, PTSA even pronounced the acicular nature of the particles, leading to increase in angle of repose.

The second group of modifiers are those with the effect on the behaviour of bulk material in such an extent that it cannot be achieved by mere control of the process's turbulence conditions – these are PSS, SLS, sunflower lecithin, dextrin, NaCMC, and bone glue. In agreement with Taylor's use of anionic dispersing agents [16], use of both SLS and PSS led to improvement in powder parameters. For SLS, the particle size was slightly reduced compared to unmodified tetrazene; however, the particle distribution is more even, the acicular shapes are replaced by diamond-shaped particles with smooth surfaces and the agglomerates are more rounded off. The addition of PSS results in lamellar crystals that however tend to agglomerate with smaller particles, giving rise to a spiky surface as compared to bone glue forming tabular crystals with smooth surface and minimal fragment and dust portions. Dextrin addition does not significantly affect the crystal habit, but improves the powder parameters by suppressing the formation of dust portions and, in general, by increasing the particle size. Similar effect can be observed in NaCMC samples, where the crystal shape is in addition to size adjustment also forced into the diamond- and flake geometry. An outlier in this group of modifiers is then sunflower lecithin, where the powder parameters are improved despite the fact that the particles are formed almost exclusively in the X shapes with rough surfaces, likely caused by embedded residues of lecithin suspension, which is indicated by elemental composition.

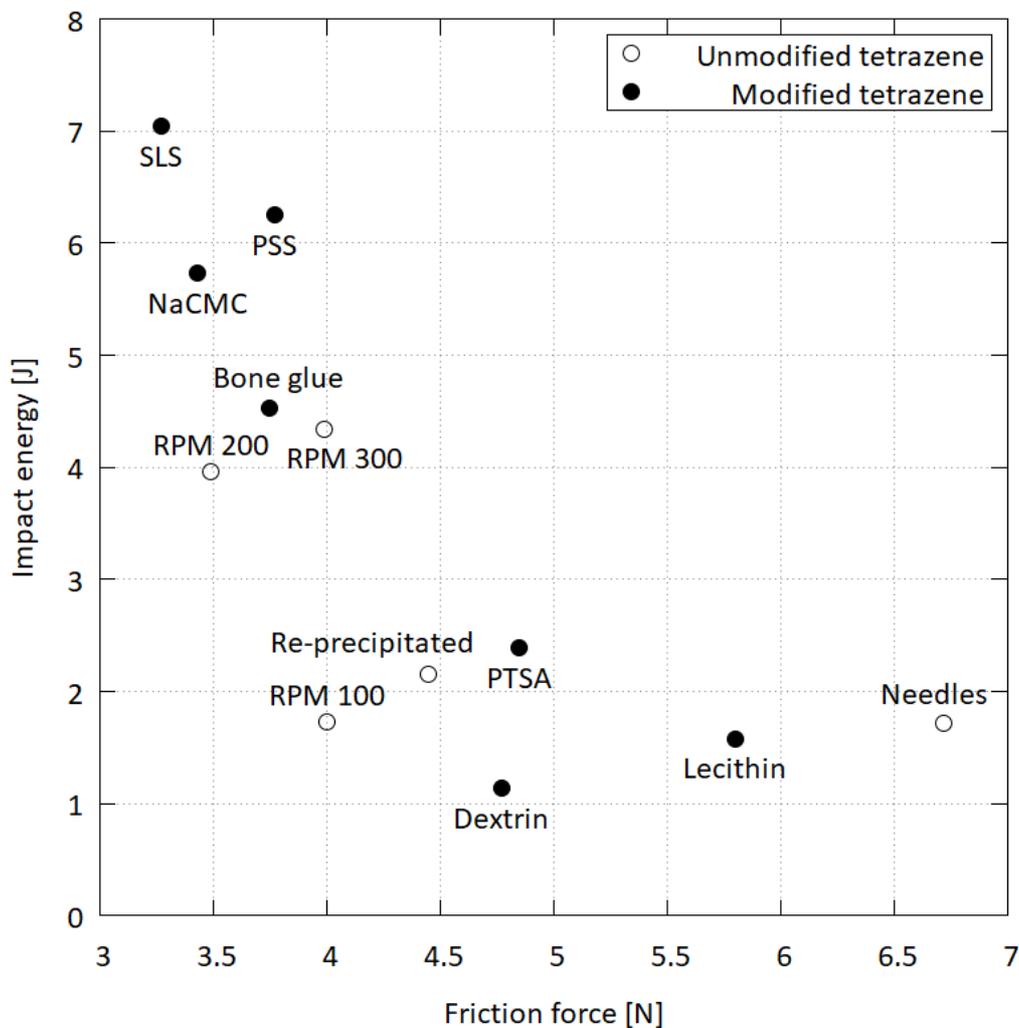
The presence of anionic moiety (PSS, SLS, PTSA) does have any effect on the crystals, but it is the rest of the molecule that governs the shape of the resulting particle. Polysaccharides either have a positive impact on the bulk behavior or none at all, depending on the individual material. As a whole there are no strong correlations between the agent structure and the effect on tetrazene crystal habit.



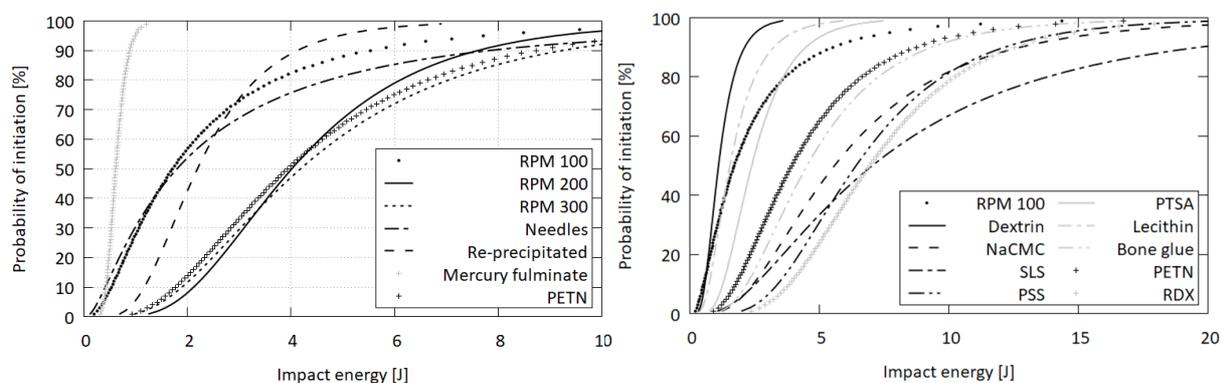
**Fig. 2** SEM images of tetrazene samples at the respective magnification

### Sensitivity

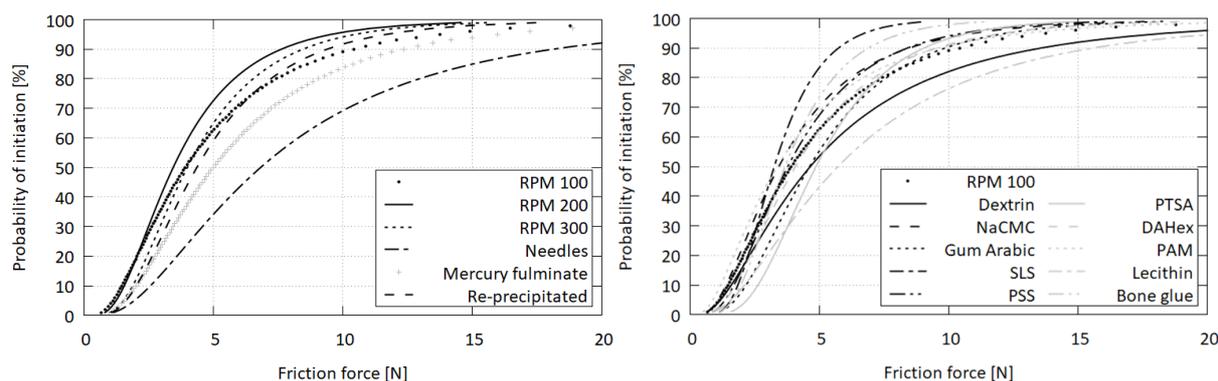
Applying a similar approach to sensitivity parameters as it was done with the powder characteristics allows one to observe any emerging patterns in the material response to stimulus. There are two areas of interest in Fig. 3.



**Fig. 3** Comparison of impact sensitivity to friction sensitivity of tetrazene samples



**Fig. 4** Impact sensitivities for unmodified (left) and modified tetrazene samples (right) Data for mercury fulminate taken from [22]



**Fig. 5** Friction sensitivities for unmodified (left) and modified tetrazene samples (right) Data for mercury fulminate taken from [22].

First grouping is the area of unmodified material and additives with minor effect on the material – they consist of lecithin, PTSA and dextrin and needles, re-precipitated and RPM 100 unmodified tetrazenes. These materials have their 50% impact sensitivity oscillating around the value of 2 J and the 50% friction sensitivity can be found in a range of 3–7 N (Table 2). It is necessary to remind that, on the scale of friction sensitivities of energetic materials, these values still put all tetrazenes squarely into the primary explosive category (pentaerythritol tetranitrate (PETN) as a reference of borderline safe secondary explosives has sensitivities of 75 N and of 3.9 J [22]). So, while the spread may seem great, within this value interval it is ultimately negligible from a practical point of view as can be seen in Fig. 5, where — with the exception of needle sample — all tetrazenes exhibit virtually the same friction sensitivities. An explanation for the decreased friction sensitivity of the needle sample can be offered via the problems with the measuring process rather than with the material itself. At low loads, the peg preferentially pushes the large particles out of its way during measurement instead of subjecting them to frictional stress, thus decreasing the apparent sensitivity. The samples falling into this category form a diverse group with no obvious correlations, as the additives range from those with major impact on crystal habit and powder characteristics (dextrin), to those with minimal (PTSA). In addition, no connection can be made with respect to the presence of modifier residues in tetrazene sample (see the results of elemental analysis in Table 1), as once again those that leave such a residue and those that do not are included in this group.

Some explanation can be found in relation to the particle size. Two studies focused on influence of the crystal size of primary explosives on their impact sensitivity have been published in the past. Both studies have shown that the impact sensitivity of primary explosive (lead azide, triacetone triperoxide) is largely independent of the individual crystals size when the sample is measured in the form of heap of crystals with uniform size [23, 24]. In the case of tetrazene, the observed differences were more noticeable.

Impact sensitivity of tetrazene is higher for a larger particle size (RPM 100) at 1.7 J and decreases with smaller particle size to 3.8 J (RPM 200 and 300), which is comparable to PETN (Fig. 4). Only these three samples can be compared as they represent the same process and can stand as a basis for comparison with modified samples. In this sense, the dextrin and lecithin samples (both of larger particle size than the base of RPM 200) follow this assumption, but PTSA then does not fit into the group. In addition, the effect of particle size alone is challenged by the fact that the coarsest (needles) and finest (re-precipitated) samples have similar impact sensitivities, when being obtained from different procedures. In conclusion, although some nuances in the sensitivity of different size fractions of unmodified tetrazene were observed, no general relationship between the impact sensitivity and crystal size of tetrazene was found.

The second area covers materials with significant effect on the material sensitivities – these include bone glue, NaCMC, PSS and SLS. Friction sensitivities of these samples, while slightly shifted toward more sensitive, are essentially the same as those for other tetrazenes (Fig. 5). The decrease in impact sensitivity by the action of these modifying agents is such that they are comparable to secondary explosives – PETN (3.9 J [22]) and even 1,3,5-trinitro-1,3,5-triazinane (RDX; 7.0 J [22]). All of these samples' impact sensitivities go against the particle size observation presented previously, as despite the generally greater particle size (which should increase sensitivity) the sensitivities were reduced. Similarly to the first group, there are no obvious connections between the additive structure and effect on sensitivities. However, in common, this group of diverse additive types have the great effect on crystal habit (compact particles without dust portions), compared to the first group where the effect is haphazard.

Lastly, there is a group of anomalous materials that are not shown in Fig. 3 nor Fig. 4 – namely gum arabic, 1,6-diaminohexane and PAM. During measurement, these samples had revealed erratic behavior, so the proper  $E_{50}$  value was not pursued. Gum arabic modified tetrazene had 1 out of 15 positive results at 2.5 J and 3 out of 10 at 50 J, placing the hypothetical  $E_{50}$  well into a range of values normally seen in substances considered insensitive, while remaining a hazardous material at lower energies; similar behavior being observed for diaminohexane. Only PAM modified tetrazene did not have any activations at lower energies, while being sensitive at 50 J with 4 out of 15 positive results. All of these additives have little effect on crystal habit despite enormous effect on the impact sensitivity; friction sensitivity remains unaffected. A partial explanation for this behavior could be the presence of terminal amine moieties in the agents, but a possible mechanism of effect is wholly unknown as neither PAM or diaminohexane stay in the tetrazene samples as significant residues, which is indicated by the elemental composition. Such irreproducible behavior is undesirable for a possibility to cause reliability issues or otherwise being hazardous for use in the final products.

The significant decrease in sensitivity of the four modified tetrazenes (bone glue, NaCMC, PSS and SLS) can be explained by two practical aspects. Lower impact sensitivity of tetrazene generally increases the safety of the manufacturing process of the tetrazene itself and subsequent processing of tetrazene into the final priming mixture. On the other hand, lower impact sensitivity of tetrazene can negatively affect the desirable sensitivity of the priming mixtures to initiation. It could result in an undesirable decrease of reliability of the primer initiation by the impact of the firing pin on the primer. Since the primer mixture is composed of a number of other components affecting highly the sensitivity of the whole mixture, it would be desirable to verify the sensitivity of the whole priming mixture.

**Table 2** Friction and impact sensitivities for tetrazene samples and parameters of sensitivity curves

Sample	Sensitivity to impact			Sensitivity to friction		
	$E_{50}$ [J]	$\mu$	$\sigma$	$F_{50}$ [N]	$\mu$	$\sigma$
Needles	1.72	0.542	1.31	6.72	1.91	0.769
RPM 100	1.73	0.551	0.932	4.00	1.39	0.772
RPM 200	3.96	1.38	0.525	3.49	1.25	0.644
RPM 300	4.34	1.47	0.573	3.99	1.38	0.580
Re-precipitated	2.15	0.766	0.506	4.45	1.49	0.605
Dextrin	1.14	0.131	0.530	4.77	1.56	0.860
NaCMC	5.73	1.75	0.704	3.43	1.27	0.739
Gum arabic (Gum)	3/15 (50 J)	—	—	4.56	1.52	0.596
SLS	7.04	1.95	0.852	3.27	1.19	0.461
PSS	6.25	1.83	0.541	3.77	1.33	0.614
PTSA	2.39	0.870	0.510	4.85	1.58	0.498
DAHex	5/15 (20 J)	—	—	4.08	1.41	0.659
PAM	4/15 (50 J)	—	—	3.38	1.22	0.802
Lecithin	1.58	0.459	0.585	5.80	1.76	0.822
Bone glue	4.53	1.51	0.605	3.75	1.32	0.507

$E_{50}$  – impact energy at 50% initiation probability,  $F_{50}$  – friction force at 50% initiation probability,  $\mu$  – mean (parameter of sensitivity curve),  $\sigma$  – standard deviation (parameter of sensitivity curve)

## Conclusions

The impact of the crystal size of tetrazene and the application of crystal habit modifiers to tetrazene synthesis on flowability, bulk density, and sensitivity to external stimuli was investigated. No evident correlation among the crystal size, flowability, bulk density, and sensitivity was observed for unmodified tetrazene.

When studying the effect of the type of modifier used for tetrazene synthesis, it was observed that dextrin, sodium salt of carboxymethyl cellulose, sodium laurylsulfate, polystyrenesulfonic acid, lecithin and bone glue have improved both, flowability and bulk density of tetrazene; in this aspect bone glue is especially notable. Gum arabic, *p*-toluenesulfonic acid, polyacrylamide and 1,6-diaminohexane have had negligible or even negative influence on flowability and bulk density of tetrazene. A strong effect of modifier on impact sensitivity of tetrazene was observed, while friction sensitivity of all the modified tetrazenes was practically intact and remained on the level of unmodified tetrazene. Tetrazene prepared using dextrin, *p*-toluenesulfonic acid and lecithin had a similar sensitivity to impact as unmodified tetrazene. Second group of modifiers - sodium salt of carboxymethyl cellulose, sodium laurylsulfate, polystyrenesulfonic acid and bone glue reduced sensitivity to impact of tetrazene to the level of secondary explosives. Although a low sensitivity would improve processing and handling safety of tetrazene it can bring an undesirable effect on reliable functionality of primer. The third group of modifiers - gum arabic, 1,6-diaminohexane, and polyacrylamide then showed erratic behavior during measurement of the impact sensitivity.

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