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SPONTANEOUS EXPLOSION OF HEXAMETHYLENETRIPEROXIDE
DIAMINE

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There are very conflicting opinions about an increase in the relative danger of large crystals of triggering explosive substances. In [1, 2] it is indicated that large crystals of lead β -azide exhibit particularly high sensitivity to mechanical effects. In [3] it is noted that large crystals of cyanurtriazide prepared with crystallization from alcohol explode on contact. The considerable danger of large crystals is explained by presence in them of thermal stresses which may lead to spontaneous explosion. In [4, 5] the authors arrive at the conclusion that the assertion of increased sensitivity to mechanical effects for large explosive crystals is hardly valid. Crystals of lead azide with a size of ~ 4 mm did not explode with breaking and crushing [4]. Taylor and Thomas tests were described which showed that occurrence of spontaneous explosion crystallization of lead azide is governed not by formation of large crystals, but by crystallization conditions. It should be noted that spontaneous explosions occur as a rule with substances whose molecules exhibit high internal energy such as azides, diazo compounds, and nitrogen halides [6].

There are no spontaneous explosions described in the literature for crystals of substances whose energy during explosive transformation is released as a result of an oxidation-reduction reaction. Therefore it might be possible to suggest that growth of large crystals of hexamethylenetriperoxide diamine (HMTD) is not dangerous with respect to spontaneous explosion. However, it appears that this is not so.

Experiments were carried out by the procedure suggested by Taylor and Rinkebach and described in [6]. In order to obtain large crystals 12 g of dry substance was dissolved in 1 liter of boiling chloroform. The hot solution was filtered through a folded filter and poured into a Dewar vessel previously heated to 65°C . The vessel was sealed by a cork with cotton threads hanging from it which served as crystallization centers, and was placed in a thermostat heated to 60°C . The cooling process to room temperature lasted about two days. After this time the cork with the suspended threads was removed. All of the threads were coated with large entirely transparent crystals with a weight up to 3.5 mg (~ 1.3 mm). This process was repeated. The crystals obtained were stable during storage and they did not explode even with breaking and crushing.

In order to grow larger crystals the Dewar vessel with HMTD chloroform solution of the same concentration and prepared as indicated above was placed not in a thermostat, but in another Dewar vessel into which 10 liters of water heated to 60°C was poured. The larger vessel was closed with a foam plastic lid and placed in a thermostat heated to 60°C . In this case the cork with the threads suspended from it was extracted from the Dewar vessel after six days. As in the previous case all of the threads were coated with large transparent crystals, and the weight of individual crystals reached 5 mg (~ 1.45 mm). Threads with crystals grown on them were spread on filter paper for drying. With careful examination of the threads extracted from the Dewar vessel it appeared that in many cases crystals grew on the thread itself and not on individual fibers as previously, and therefore threads passed within crystals. In addition, the thread itself was easily broken away by weak force.

Approximately five minutes after extracting threads from the mother liquor in attempt to remove crystals there was explosion of several crystals, and not every thread nor those crystals which were being removed exploded, but those which lay freely on the filter paper and were not subjected to any action.

Approximately ten minutes after the first explosions there was spontaneous explosion of several crystals on threads lying calmly on the filter paper and judging from the traces re-

maintaining on the paper every thread exploded, but only for individual crystals. Threads beside an explosion were thrown to the side. Crystals on them did not explode or ignite.

In order to prevent further spontaneous explosions all of the scattered crystals (~3 g) were collected and poured into a liter beaker with cold water. During collection of crystals scattered over the laboratory there were individual explosions when crystals which fell on the linoleum floor covering were stepped on by accident.

Individual weak clicks were heard one to two minutes after placing the crystals in water, and then there was a strong explosion. Glass fragments punctured a glass vessel standing alongside. The tiled plate on the which the beaker stood was cracked. It was noted that HMTD crystals remaining in the mother liquor for two hours after removing the threads did not explode. Then the Dewar vessel with the mother liquor and crystals was disposed of.

Currently it is difficult to explain the reasons for spontaneous explosion of HMTD crystals not only in water, but also in air. However, it is possible to suggest that explosion occurred due to cracking of crystals held for a long time in the mother liquor under the action of internal stresses occurring in them with expulsion of volatile-solvent residues in them.

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