

Letters to the Editor

Safety and Environmental Report

To the Editor: Pyridinium Dichromate Runaway in a Populated Work Area

Sir: Recently we investigated for one of our customers a runaway reaction of 15 kg of pyridinium dichromate (PDC) during repackaging. Owing to this incident personnel were exposed to PDC, and a large area had to be decontaminated.

The Incident. Pyridinium dichromate was delivered in small drums, containing 15 kg of PDC each. For production the required amount was weighed and repackaged in three stainless steel 50-L corrugated drums, each containing 15–19 kg of the product. The lids on the drums were closed with clamping rings and stack-piled.

Repackaging took about 45 min at ambient temperature (about 20 °C). Approximately 1 h later the first drum (lowest in the stack) started to hiss. Within a few seconds the lid flew open and a blue flame emerged accompanied with a lot of green smoke. The force threw off the drums on top. The resulting fire could be extinguished with water. A few hours later, the (middle) drum originally placed on top of the lowest drum started to leak gas and green solids as well. Immersing the drum in water could stop this. The third drum (top) remained undamaged.

Incident Investigation. The operation was not new to the customer and had been carried out since 1994. The stainless steel drums were used for weighing out products and were thoroughly cleaned and dried afterwards.

This incident happened with a first delivery of a new supplier. Interviewing the operator made clear that the decomposed material had a different appearance from normal: instead of free-flowing orange crystals the product was orange-brown and compacted to a big lump.

Using a Tripod analysis two possible causes were defined: (1) low quality and high instability of the batch, as

supplied and (2) different quality of PDC, possibly in combination with a contaminant.

A low PDC stability as such was not likely, as the product had been in storage for some time without causing problems. Repackaging the product was considered to be an important parameter in the cause of the incident. The presence of water was highly unlikely, but it could not be excluded completely.

Several contamination experiments with water and PDC (from the same lot but from a different container) were performed. Neither gas evolution nor a runaway reaction could be initiated. Also differential scanning calorimeter (DSC) experiments were performed on the PDC from the incident lot and compared with regular PDC from another supplier. The only difference that could be established was a small endothermic peak in the area around 100–120 °C that was present in the incident lot only.

The decomposition of the second drum was attributed to the heat development of the first decomposition in the drum standing underneath it.

Remaining Questions. Although we have investigated this incident thoroughly, we were not able to find a probable cause. Although we had some indications that the PDC involved was of a different quality, this could not be proved as all material from the original drum had decomposed in the incident.

PDC is generally considered to be a stable product at room temperature. Because of this incident with considerable health and safety consequences (fire, contamination with Cr(VI)) we would like to get into contact with anyone who has experienced a “spontaneous” decomposition of commercial PDC at room temperature or knows conditions under which such a decomposition could be initiated.

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