

SHELL DEVELOPMENT COMPANY

REFERENCE

931
El Paso
0'00
Ag Chem -
Qin
origin

DATE NOVEMBER 10, 1976

TO SHELL CHEMICAL COMPANY
SAN RAMON
MANUFACTURING-PLANT & ANAL.-
PROJECT COORDINATOR-EL PASO

FROM DEPARTMENT HEAD-FORMULATION/
COMMERCIAL FORMULATION SERVICE-
BSRC-MODESTO

SUBJECT MINUTES OF SAFETY DESIGN MEETING
EL PASO PLANT; OCTOBER 20-21, SAN RAMON

Per your request, your draft of the minutes of the October 20-21 meeting at San Ramon covering discussions of safety in grinding facilities at the El Paso Plant is returned with comments inserted on the margins by the Modesto attendees. We are in agreement with the recommendations as set forth there including our margin inserts. Some additional comments follow.

In reviewing the safety features of this plant, it becomes of primary importance for all areas of the company to appreciate both now and in the future that this facility is a special purpose grinding facility. It does not have the safety features for grinding materials that have a greater dust explosivity hazard than BLADDEX® Herbicide.

We recommend close attention to the flammable vapor (DMK) content of the technical herbicide as introduced into the blending facility of the plant. Per the discussions we agree with the proposal for close surveillance of the incoming feed for its solvent content. As this monitoring apparently will be on a manual inspection basis, we raise the advisability of a flammable vapor alarm system for the units which precede the inerted grinding loop.

An unknown which could have significant impact on safety design parameters is the level of flammable volatiles given off in thermal decomposition of BLADDEX or atrazine. We are in the process of determining these and will keep you current with our findings.

As you are aware, the BLADDEX dust explosivity characteristics which are critical to the safety design of the plant have been determined necessarily on material other than Mobile production. It may be prudent to recheck the values of critical importance as soon as this material becomes available in order to provide confirmation of the design basis.

We appreciate the participation in these discussions, and regret the delay in returning this memo.

Original Signed by
G. W. GAERTNER

G. W. GAERTNER

LAM 027518

Attachment

cc: Shell Chemical Co., San Ramon
Information Services (2)

PLAINTIFF'S EXHIBIT

SH-1785

ABS-009773

DRAFT

Shell Development Co. Modesto	
DATE	OCT 27 1976
BY	7510-76 A1
BY	EWG

MINUTES OF MEETING

San Ramon

October 20-21, 1976

Attendance - per attached list.

Purpose:

To review the design of the El Paso formulation plant and the Mobile triazine plant concerning safe handling of triazine dust and powder, especially with new explosivity and thermal decomposition data. To reconcile a proposed BLADEX® grinding safety guide and the above designs. The attached Agenda was followed.

Results

New explosivity data for more finely ground herbicides, i.e., BLADEX and atrazine wettable powders--while not correlating well theoretically with earlier data--indicate that the explosivity factors are of the same order as for earlier data. ✓

The heat of decomposition of BLADEX appears to be about 25,000 (by WRC) calories/gram mol exothermic, enough to raise the temperature 347° adiabatically, excluding melting. Differential thermal analysis indicates that up to 200°C "other ingredients" do not affect BLADEX decomposition. Slow and mild exothermic decomposition occurs above or beyond 200°C for W.P. and 240°C for technical BLADEX. Atrazine is in same general range. Little is known about decomposition gases--no HCN has been observed so far--more work is needed. Detailed reports will follow; preliminary presentations are attached. ✓

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Residual acetone concentrations of above 0.02% w can lead to explosive mixtures above 100°F. The current specification of 0.05% w

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volatiles, as acetone in BLADEX should be revised. In practice, product runs under 0.01% w, at El Paso incoming feed--especially in tote bins-- should be monitored for acetone content or explosive atmosphere. Mobile will strive to avoid such. *(sample sent to Hi)*

"Commercial incidents" - thermal decompositions in BLADEX formulation are documented in the attached reports from Helena Chemical and a Modesto Trip Report. A recent thermal decomposition at DEGUSSA's technical BLADEX manufacturing facilities occurred in product drying. In all instances there were no reports of poisonings, injury or significant damage to facilities. Causative explanations may be:

- a. Operating with a blocked hammer mill.
- b. A piece of metal in a hammer mill - tearing screens - overheating extending to product.
- c. Overheating in a product drying system - (DEGUSSA) possibly exacerbated by some impurity.

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No explosion incidents have been reported to date. There are no confirmed incidents regarding atrazine, only rumors of GEIGY decompositions. Mechanisms and sources of overheating or electric discharge were discussed; concluding the following:

Herbicide powder, ^{on free into} falling ~~down~~ in a bin, is not likely to develop a spark potential exceeding 100 milli-joules; ^{this value is} well below that needed to ignite ^{to blades} dust clouds per attached data. Ground powder, flowing in grinding loops, will gain heat from hammer-milling and may gain static charge flowing in the loops; ^{again the static charge is not expected to reach 100 mv and these systems are inerted in addition.} A piece of metal, coming loose in the system - or escaping detection, etc. - ^{It has been postulated that} falling free in a large bin or rotating within a ribbon blender will not heat or develop a spark intensity sufficient to cause

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aid could provide a source for initiating thermal decomposition, this decomposition proceeds in the absence of oxygen as well as when inerted.

low pressure,
high temperature?

1 - 3 -
inert?

E ? JF

Tight seals on rotating shafts as in star valves, feeders,

screw conveyors and ribbon blenders are sources of heating. However, the heat is removed considerably by the flowing powder and metal mass; In a ribbon blender the charge moves over the hot spot drawing off the heat.

(Some ribbon blenders will have water jackets.) Blender M-1028 at El Paso may hold from 5,500 to 13,750 lbs. of wettable powder feed - has a 75 HP drive - if all energy put-in converts to heat 191,000 BTU/hr. and is held adiabatically, the theoretical temperature rise is 115 to 46°F/hr. Product melts at 325°F. and decomposition starts at 392°F. There will be heat loss and melting will absorb heat. A blocked-in ribbon blender with or without tight shaft seals will heat up slowly. With extended mixing it needs watching for possible overheating.

2

typo error
here?
No X -
OK H

The tendency of triazine powders to develop and to bleed off static charges is not known quantitatively or relative to other materials. Some measurements should be attempted by Shell Development to orient on this aspect. Electric grounding in bag houses, bins, lines, ducts, etc. is being provided and will be scrutinized for adequacy of electrical connections.

The El Paso design for powdered formulated product manufacture and handling and for building air/vacuum clean-up systems was reviewed in detail and was accepted as satisfactory subject to some items below.

By way of quick review, the design calls for:

1. Nitrogen tempering (reduced oxygen) of the gas circulation in each of the three hammer-mill grinding loops (includes oxygen analyzers and alarms).

2. No nitrogen in receiving or weigh bins, in feed-preparation ribbon blenders, product blenders "sack-off bin" or bagged feed slitting.
3. Electric grounding throughout.
4. Dust proof electrical systems, NEMA 12.
5. Magnets at strategic points with full metal detection and feed cut-offs at hammer mills.
6. Indoor bag houses with electrically grounded bags.
7. No rupture discs with large vent headers. **LAM 027522**
8. Fire hoses and extinguishers at strategic points.

Items to be added and/or pursued are:

- A. Make certain ducts are electrically bonded.
- B. Put hose connections and manual shut-off valves on all ^{and solids handling} major "dust" equipment or where a significant amount of dust can occur. Provide hose reels conveniently. Provide self-contained air masks to permit coping with fumes from a decomposition or overheating *or a major dust release.*
- C. Add gas purge on seals where erosion by powder is probable.
- D. Check unit heater motors for adequacy in dusty atmosphere. Correct any problem - use fresh air blanketing if need be so.
- E. Check sandmill "drip-proof motors" for compliance with dust-proof criteria. Correct if problem exists.
- F. Set up inspection incoming totes and grinding loops for presence of acetone. *Install a flammable vapor alarm in feed hoppers?*
- G. Provide temperature alarms in gas leaving heat exchangers in grinding loops to warn of poor or no cooling.

- H. Provide thermometers on hammer mills to catch any local heat buildup for whatever reason.
 - I. Provide for grinding loop automatic shutdown when the secondary filter has a high pressure drop.
 - J. Provide grinding loop pressure relief - protecting against over-pressuring by blockage, excessive nitrogen, etc.
 - K. Avoid skin temperature in building air (unit) heaters which melt or would decompose the triazines.
 - L. *Change O₂ secondary alarm to alarm + shut down.*
- Mobile and Vicksburg were also reviewed with limited information

on the latter. No difficulties arose re Mobile. Vicksburg should be advised of our safety concepts.

The proposed safety guide and an amended version, more applicable to BIADEX® and to atrazine, were reviewed. It was concluded that the proposed guide should be called a "general purpose pesticide grinding guide" as it was intended and was used originally for materials more sensitive than the triazines and by formulators considered much less skilled and diligent than the Shell plants. Copies of the relevant passages under consideration are attached. The differences are highlighted in that the general guide calls for:

1. Nitrogen tempering of air whenever BIADEX or atrazine is processed instead of only in grinding loops. LAM 027523
2. Outdoor location of bag houses - (suitable in warm southern climates).
3. Water addition by spray headers with remote activation versus plain hose connections.
4. Large blow-out rupture discs with vent-off headers. ABS-009778

for grinding Shell Pesticide
as on all purpose instruction to contract formula
which should present safety
recommendations

It was agreed the general guide would be re-written ~~and~~

It will submitted to Safety and Health before Operations & Distribution use it
in obtaining custom formulation work.

Toxicology reported that acute inhalation studies with ground
BLADEX® showed no untoward effects so far - all test animals had not been
examined. Measures to keep air clean down to 10 mg. and better yet 5 mg/
cubic meter should not be relaxed.

Noise control is not overlooked but difficult to tackle till
the specific arrangements have been constructed.

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