

Shell Development Company
Westhollow Research Center
January 9, 1978

MEMORANDUM OF DISCUSSION

Location: Denville, N.J.

Date: December 15, 1977

Participants:

Hazards Research Corporation - Dr. Chester Grelecki-Chief Scientist
- Steve Tunkle, Chemical Engineer

Shell - B. I. Sparr, Shell Development Co., Modesto
P. V. Jennings, Shell Development Co., Modesto
M. S. Honig, Shell Chemical, Houston
R. A. Page, Shell Chemical, El Paso, Ill.
R. B. McAulay, Manufacturing - Safety and Health, Houston
C. Lindauer, Shell Chemical, Denver
C. R. Garbett, Shell Development Co., Houston

DISCUSSIONS ON SAFETY IN POWDER HANDLING SYSTEMS

The discussions with Hazards Research had been organized to review potential problems in handling agricultural dusts of-wettable powder formulations, especially related to equipment nearing startup in Shell's new El Paso facility. The writer was included for possible input, and to get pointers from Grelecki's wide experience which could be useful for many other solids handling problems in the company.

Hazards Research Corporation

The company was formed to take over the facility vacated by Thiokol's Reaction Motors Division at the termination of their government contracts for developing solid-fueled rocket motors. It occupies a semi-remote, wooded, hilly area very near Picatinny Arsenal, and retains many of the bunker and explosion test facilities left over from the development of solid propellant technology. Dr. Grelecki himself worked with Thiokol.

Pages from their brochure, reproduced here, describe their activities. The firm is a small private one with 15 (or so) employees. In addition to Grelecki, Tunkle, whom we met, the staff includes William Cruice, a chemical engineer; George Patino, a mechanical engineer who runs their dust experiments and does structural analysis (for resistance to blast forces); Bob Putnam who is a PhD organic chemist working on organic processes, design of experiments; and about 6 mechanics and technicians.

Part of the discussion related to specific identification of potential hazards in handling particular agricultural chemical dusts. No attempt is made here to report on these questions. However, much of the discussion was general on the hazards of dust conveying and handling systems, and some of the specific comments should be of widespread interest. They are set down here in random order.

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Personal Remarks on Dr. Grelecki

Over the years Dr. Grelecki has accumulated a tremendous variety of experiences on the causes and hazards of dust explosions. Typically, he will make a statement of a fundamental principle or describe some basic phenomenon (usually with simplicity and clarity), and then proceed with a rich succession of anecdotes that illustrate or support his point. He is full of practical-minded advice and rules of thumb for guidance in common problems. He is open about telling what he knows, and careful to qualify what he doesn't know, or where information is dubious. His basic philosophy is a very conservative one; hazards should be judged weighing risks against possible consequences, and when the risks of substantial damage are high, the hazards should be controlled to very low levels; there is no such thing as zero risk.

Grelecki conducts a two day AIChE seminar on "Fundamentals of Fire and Explosion Hazards Evaluation", which the writer had attended, and which is hereby recommended to anyone in Shell having to deal with problems of possible explosion hazards.

General Remarks on Dust Explosions

Ignitability, Combustibility

The concentration limits for combustion of organic dusts in air are usually lower than for gases or vapors. Rule of thumb:

- Dusts: LFL = 25 mg./l.
- Organic vapors: LFL - 50 mg./l.

This arises from the heterogeneous nature of the dust-in-air (i. e., the effective fuel concentration next to the dust particle surface is high).

Effects of Particle Size

The mass consumption rate of the dust flame is very much affected by the particle size, the rate being proportional to the surface area. Commonly flammability data is given for dusts of a specified size or size distribution, but this is not enough. The important factors are the surface area and the "web thickness", which is half the thickness of a flake, or half the diameter of a needle-shaped particle, or half the diameter of a spherical one. (The web thickness governs the time that it takes for a combustion reaction to proceed through from the surface.) Thus, two nominally similar dusts can have strikingly different explosion characteristics if they are made in such a way as to give different particle shapes. For very fine dust particles, at the lower limit, dusts act like vapors; but there is no sharp changeover at a limiting size.

Ignition by Hot Spots

Ignition is affected by the nature of the "hot spot" - the temperature, the size, and the duration of exposure. This explains why there is so much variability in data on ignitability, and one must resort to standard test procedures, such as the USBuMines tests in the Hartmann apparatus. Unfortunately, the actual exposure condition in a plant may differ widely from the special test condition. One should rely on these test results primarily for comparison

with materials of known and familiar properties and behavior. Too close a reliance on test data for design without plenty of margin is likely to lead to trouble (e.g., explosion pressure rise rates for determining peak pressures in a vented vessel).

Moisture (water) present in the dust can have an appreciable effect on the explosibility of a dust. Rule of thumb: If the percent moisture is equal to or greater than the percent dust concentration, the mixture won't burn (in air). (Moisture is also important for static charge effects, see below.)

Presence of even very small amounts of organic vapors in the dust system can dramatically increase the explosive hazard. Presumably, despite the overall low concentration, the organic vapor adsorbs on the dust particle surface where burning proceeds.

Problems with Equipment

Sizing of Vent Area

Requirements for venting of enclosed equipment are very poorly dealt with in presently available US codes and standards. Grelecki recommends using the data developed by Bartknecht of Ciba-Geigy, which have been incorporated in VDI Guidelines 3673, "Venting of Dust Explosions". These guidelines are in German, and Grelecki gave us a copy of an English translation. The guidelines are currently being incorporated into revised recommendations of the NFPA, but the revisions are still in process. The VDI-Bartknecht procedure uses the rate-of-pressure-rise from tests of a particular dust and the size of the test chamber to determine a constant, K_{st} (the VDI test chamber is 1 m³ sphere). Nomographs are provided for sizing the vent area required to limit the relieving pressure in the vessel to a particular maximum.

Scaling for equipment size is based on

$$K_{st} = \frac{dp}{dt} (\text{Volume})^{1/3} = \text{Constant}$$

The data applies to vessels of near-sphere shape, with ignition near the center; the scaling law implies that the flame spread velocity remains constant, regardless of vessel size. Long, narrow vessels and ducts can react differently because of convective movement of burning material which increases the effective burning rate. Ducts should be provided with vents every 10 diameters (unless they are designed to contain the explosion pressure).

Grecki very strongly emphasizes that every piece of equipment handling flammable powders (even those classed as "Weak" in explosivity) should be provided with explosion relief vents, unless it is designed to contain an explosion. Even though the likelihood of an explosion appears to be very low, there is enough uncertainty that the possibility of an explosion must be recognized; failure to do so would put the plant operator in an indefensible position if someone were to be hurt by the rupture of an unvented system.

Grecki noted that vents sized on the basis of the USBuMines Hartmann test chamber values for rate of pressure rise would be unnecessarily large, and that the sizing should be scaled holding K_{st} constant, giving dp/dt proportional

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to the inverse of the cube root of the scaleup volume ratio. The Hartmann test gives the most rapid dp/dt and the "worst case". Vents should be sized to hold the maximum explosion pressure to below $1/4$ the rupture pressure of the vessel or duct or silo.

Controlling Electrostatic Charge Buildup

Humidity is important in the extent to which electrostatic charges may develop; but the effect depends a lot on the particular material. The water molecules can form a conductive monolayer on the surface of the dust particle, and this layer can form a conductive path, particle-to-particle, to bleed off the the accumulated charge. Rule of thumb: Electrostatic charge buildup on an accumulation of powder is generally not a problem if the relaxation time for bleeding away the charge is less than 0.2 sec; this corresponds roughly to a conductivity of a bed of material of 10^{-12} mho/cm, about the same as required for liquids.

Conductivity of packed powders can be measured; Hazards Research has laboratory equipment for doing this on samples supplied by clients. Conductivity can be increased by gamma radiation; 3M market equipment for doing this.

Bonding of Ductwork and Equipment

If there is any question that bonding may be deteriorating due to corrosive plant conditions, etc., the bonding should be checked periodically by continuity test. On aluminum ducts, it is common to use straps that have sharp points embossed in them which are intended to penetrate paint, oxide layers, etc. to obtain electrical contact.

Fluid bed dryers develop high ES charges in the bed (they sometimes glow in the dark from the corona discharge). Normally the potential is from particle to particle, and there is no sharp gradient to the container wall that would give a spark discharge.

Baghouse filters often give spark ignition sources when the bag support cages are not properly grounded. It is common practice to fold the bag around the collar at the end of the cage to make a dust-tight gasket, which then acts as an electrical insulator. Then, when cyclic pulsing is used to dislodge the accumulated dust, there will be different charges on adjacent cages, with the possibility of spark discharges from one cage to its neighbor, or from cage to ground.

Hammermills provide one of the most common sources of ignition in powder systems. Tramp material entering the system is usually the culprit, but bad bearings and seals overheat and give ignition.

Conveyors, especially elevating conveyors, are perpetual bad actors. Each drop on and off the conveyor yields dust clouds; bearings fail; chain drives fail and jam; friction leads to electrostatic charge buildup. Grelecki recommended that wherever possible conveyor runs should be interrupted with choke points to arrest passage of flame from one part of the system to another. Flights or drops from one section to another should terminate in a hopper that is always partly filled with powder. Screw conveyors should have its screw flight interrupted, once every 10 diameters, so that powder will accumulate and block the passage. (These arrangements could lead to difficulties with sticky or non-free-flowing materials).

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Cryogenic grinders using liquid nitrogen as coolant and inerting gas were found to be in trouble on one occasion from condensing out liquid air; subsequently the nitrogen boiled off, leaving a residual rich in oxygen. Mill friction in the presence of the oxygen resulted in a fire.

Grelecki's comments, suggestions, recalled instances, came thick and fast, and there were many more than what hastily written notes can bring to recall.

ChRG:mdb

Attachment

cc: B. I. Sparr
M. S. Honig ← THIS COPY FOR-42
R. A. Page
R. B. McAulay
P. V. Jennings
C. Lindauer
G. D. Towell
J. C. Dygert
C. D. Merdian
W. C. Bluhm
W. G. Gottenberg
W. R. Harp
D. R. Grabow

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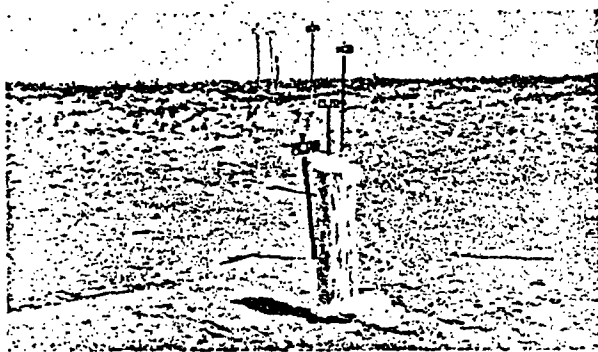


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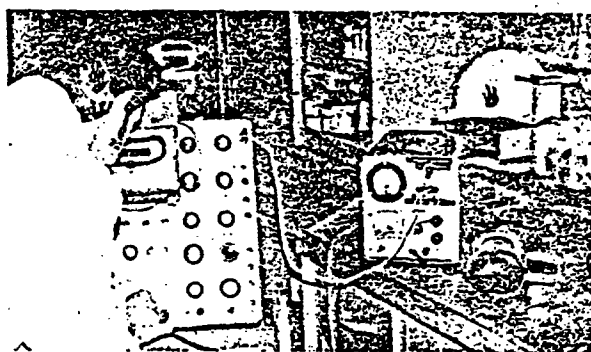
Explosions and fires constantly plague the chemical industry, frequently resulting in substantial loss of lives, property and business opportunities. Yet, the frequency of these incidents can be reduced and their effects minimized through analysis of the hazards of fire and explosion inherent in most chemical processes.

HAZARDS RESEARCH CORPORATION was formed in 1969 to afford expert technical consultation, laboratory and field test services to commercial and government agencies faced with problems in chemical fire and explosion hazards. It has since performed over one hundred different programs for more than seventy clients. Field studies have been conducted at plants in Texas, Alabama, Virginia and Turkey; studies performed at HRC facilities have been sponsored by clients throughout the United States, Europe and Asia. Applications range from cosmetic solvent evaluation, to aerospace propellant safety. . . from petrochemical processing, to disposal of hazardous waste materials.

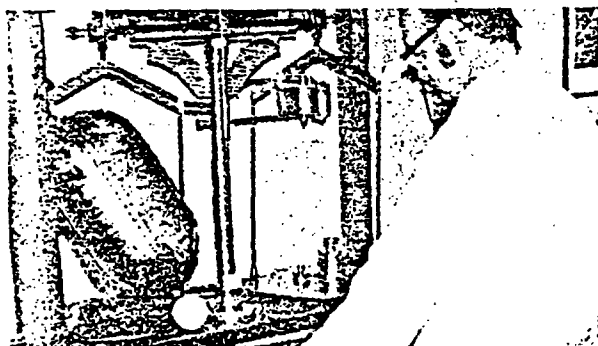
HAZARDS RESEARCH CORPORATION is owned and operated by technical personnel directly engaged in the field, and is not connected with any enterprise other than evaluation and research on flammable and explosive materials. The staff is composed of a small group of specialists, each having extensive experience in combustion and detonation phenomena and the hazards of processing, storing and transporting reactive chemicals. The organization enjoys an international reputation and is recognized as an authority in the field by both professional and governmental agencies.



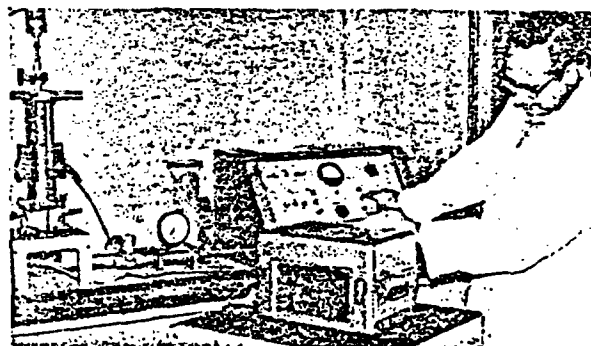
Large Scale Explosive Output Tests



Detonation Velocity Measurements



Precision Gas Mixture Preparation



Dust Explosion Pressure Measurements

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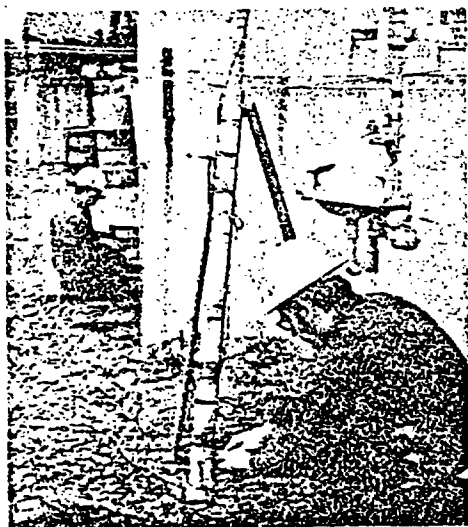
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CAPABILITIES

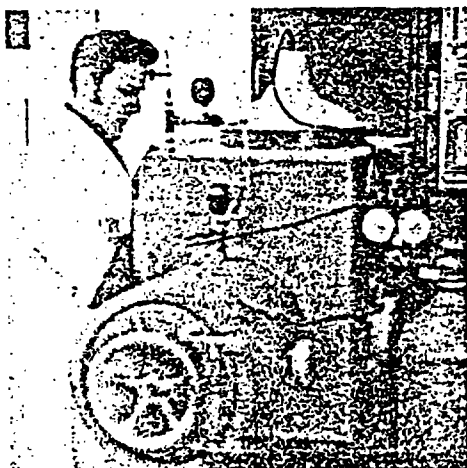
The technical staff and resources of Hazards Research Corporation are geared to provide expert consultation and research services in the following:



Custom Thermal Explosion Experiments



In-Plant Gas Flame Velocity Studies



Controlled Atmosphere Sample Handling

Preventive Engineering

Process Design Safety Review and Analysis
Protective Systems and Structures Development
Electrostatic Accumulation Studies

Laboratory Research and Testing

Shock Sensitivity and Detonability
Thermal Explosion; Autoignition
Vapor Flames; Gases, Mists and Dusts

Field Service Applications

On-Line/On-Site Process Stream Testing
Gas Detection and Monitoring
Blast Effects Investigation and Analysis

Pilot Plant Services

Process Element and Equipment Testing
Relief and Suppression Systems Evaluation
Unit Operations; Remote or Automated Handling

Auxiliary Service Operations

In-Plant Seminars; Short Courses
Qualification of Products for Transport and Use
Disposal of Hazardous Materials

FACILITIES

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Hazards Research Corporation is located in northern New Jersey, convenient to transportation facilities of the New York Metropolitan Area. The complex is properly isolated to permit considerable freedom in handling energetic materials.

The laboratories are equipped for high and low speed recording, high pressure, vacuum, and high and low temperature conditioning and testing. Mass, volume, pressure, temperature and flow measurement units, isolation chambers, dry boxes, process components, and glass and metal systems are on hand. Gases, liquids, solids, mists and dusts are routinely handled in standard or custom equipment.

The staff of Hazards Research Corporation cordially invites your inquiries to explore the full range of potentially dangerous situations your process may involve. In-depth conferences may be held at HRC facilities or at your plant, according to your needs. All inquiries and services are strictly confidential.

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DR. CHESTER J. GRELECKI

President and Chief Scientist of HAZARDS RESEARCH CORPORATION, PH.D., Physical Chemistry, Catholic University of America, M.S. Duquesne University.



Co-founder of the Fire and Explosion Hazards Evaluation Service at Thiokol Chemical Corporation's Reaction Motors Division, Dr. Grelecki was Chief Scientist of that service from its very inception. During this period, Dr. Grelecki became Manager of Research Operations, responsible for work in organic and inorganic chemistry, analytical methods development, polymerization processing and combustion engineering, in addition to his work with the Fire and Explosion Hazards Evaluation Service. Previously, as Unit Supervisor, Advanced Physical Chemistry Research, Dr. Grelecki had pioneered work in detonation velocity and critical diameter measurements, shock sensitivity determinations and the thermal explosibility studies on a wide variety of rocket propellants, process mixtures and commercial chemicals. A member of the American Chemical Society and the Inter-agency Chemical Rocket Propulsion Group's Committee on Liquid Propellant Test Methods, Dr. Grelecki also serves as Vice-Chairman, ASTM Committee E-27 on the Hazards Potential of Chemicals. He has authored over fifteen publications in the fields of kinetics, free radical chemistry, propellant chemistry and safety.

WILLIAM J. CRUICE

Senior Technical Associate of HAZARDS RESEARCH CORPORATION, M.S., Physical Chemistry, St. John's University.



While at Thiokol, Mr. Cruice was responsible for general technical and administrative management of Fire and Explosion Hazards Evaluation Service at Reaction Motors Division. Mr. Cruice engaged in technical consultations and experimental design of all test programs. In addition to his supervision of experimental work, Mr. Cruice designed equipment for customized tests, supervised its construction and documented its application for presentation to technical societies. Prior to his activities with the Fire and Explosion Hazards Evaluation Service, Mr. Cruice conducted theoretical and experimental studies to determine kinetics and reaction mechanisms for the thermal decomposition of advanced solid oxidizers. He also participated in advanced research and feasibility studies in the areas of corrosion and heterogeneous catalysis, propellant chemistry, and incendiary agents. Portions of his work have been published in *Advances in Chemistry* (1966). Mr. Cruice is a member of the American Chemical Society and the American Institute of Chemical Engineers, and has served as a subcommittee vice-chairman on ASTM Committee E-27 on the Hazards Potential of Chemicals.

FOR A CONFIDENTIAL DISCUSSION on your fire and explosion problems and how HRC can assist you, write or call:

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