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PREFACE

Dow's *Environmental, Health & Safety Requirements* state:

"Each location shall have an appropriate and active reactive chemicals program. Regular reviews of process reactive hazards shall be required for existing processes, new processes and whenever key personnel or a process is changed, as well as a thorough review of laboratory or pilot plant data prior to scale-up."

This guideline is intended to be a resource for persons wanting to learn more about Reactive Chemicals. The information here is intended only to provide guidance on "how to" and is not intended to be a "requirements" document. For the detailed requirements for Reactive Chemicals, see the *Global Reactive Chemicals Standard*.



Global Reactive
Chemicals Standard

PURPOSE

The purpose of the Reactive Chemicals Program is to prevent uncontrolled chemical reactions which have the potential to result in injury, property damage or environmental harm. This can only be achieved by having a thorough understanding of the chemistry and processes that we work with and a disciplined approach to operations and process changes.

INTRODUCTION

The control of chemical reactions is our business. Through the control of reactive chemicals we manufacture nearly all our products. Normally, we carry out these reactions without incident or mishap. However, occasionally chemical reactions get out of control because we use the wrong material, change operating conditions, have unanticipated time delays, have equipment failures, or because we don't always completely understand the chemistry of our process.

Chemical reactivity is a very complex phenomenon, and there are no substitutes for education, training, experience and good judgment in evaluating the potential hazards. Therefore, it is essential that a reactive hazard evaluation be made on all processes on a periodic basis. These evaluations/reviews should be supported with basic data or analysis of the reactive properties of the chemicals and the mixtures being used.

Reactive chemicals within Dow is a multi-disciplined effort that brings together people and resources with broad technical and experience backgrounds. The basic goal is to deliver effective consultation and guidance to the people in the facilities and technologies that are producing or handling products, or are developing new processes and chemistries. Utilization of this breadth of knowledge and background yields much better consultation and support than if reactive chemicals were to be delivered by a single discipline. The primary discipline partners in this effort are: Research (both analytical and process research), Technology Centers, Process Engineering and Process Safety, which leads the coordinated efforts. Other disciplines and expertise should be involved, as appropriate, in the process depending on the reactive chemicals issues being addressed.

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KEY PRINCIPLES

A multi-functional Global Reactive Chemicals Steering Team identified three key principles to guide our overall reactive chemicals effort. They are:

1. Reactive Chemicals at Dow plays a key role in avoiding circumstances that put people, environment, equipment or businesses at risk.
2. The focus of the Reactive Chemicals Program is the understanding of the inherent energy of our systems and conditions under which it can be released. (This includes the understanding of all the potential hazards that may exist. It is important to understand that a reactive chemicals event does not have to be a violent fire or explosion. In reality, the reactions can be slow and still result in injury, loss or environmental damage.)
3. The "Keystone" of the Reactive Chemicals Program is the concept of "Owner Responsibility." (When all the advice and consultation is gathered relative to an issue, it is the process or facility owner's responsibility to make the correct decisions. It is recommended that the "Owner" be defined as the person who approves the highest level of Management of Change for the facility.)

HOW TO APPLY REACTIVE CHEMICALS

A. Research

The researcher, by the very nature of his/her work, must constantly deal with chemical reactivity and determine the appropriate time to obtain reactive chemicals data. Obviously, each reaction mixture or minute quantity of unknown material cannot be subjected to extensive testing for reaction potential. On the other hand, uncontrolled laboratory reactions which injure people and damage property must be prevented.

The following general guidelines are designed to help the researcher minimize uncontrolled reactions:

- Know the properties of the chemicals being used and their potential for uncontrolled reaction.
- Provide protection from the possibility of unexpected reactions with suitable laboratory facilities and shielding.
- Keep quantities of materials to a minimum, scaling up gradually with appropriate safety precautions.
- Obtain reactive chemical screening data as a research project progresses.
- When other persons or groups become involved, be sure that adequate hazard information is developed and transmitted to them.
- Make sure that appropriate use is made of the Reactive Chemicals Review Processes.

It is not possible to establish the exact point in a research project when the screening tests outlined in this guide should be used. (R&D safety manuals often provide additional guidance on this issue.) The persons working directly on the project are the ones who can effectively evaluate and control this need. In general, no research project should be pilot planted unless a reactive chemicals review is held. The level and depth of review will be driven by the amount of reactive chemicals potential risk present in the project or process. Higher risk projects should be reviewed sooner in their development process, sometimes the review is appropriate at the laboratory scale. R&D Core Analytical and Process Safety focal points are available to provide consultation and advice on the best time to have a review for a given project. The R&D Core Analytical groups have a variety of tools to help evaluate and predict the thermodynamic potential for the proposed work even at the conceptual stage. If a Technology Center exists for the researched project, they should be consulted on the review recommendations as well. There is often an opportunity to combine reviews to be more efficient. The "Early Stage Review" process and Technology Center Review process should be evaluated for opportunity to combine reviews with Reactive Chemicals.

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B. Production and Pilot Plants

- New Processes

Raw materials, process streams, products and waste of any new process that has reached the pilot or production plant stage shall be reviewed and evaluated to determine if any potential reactive chemical hazards are involved. The "Functional Input and Evaluation Process" provides guidance on when new facilities should have the appropriate reviews. (See the Global Project Methodology web site (<http://intranet.nam.dow.com/gpmrc/gpmhome.htm>) for the Functional Input and Evaluation Process manual.)

In general, if insufficient data are available, then the materials should be subjected to screening evaluations or tests. A reactive chemicals review and concurrence should occur prior to project capital authorization.

- Established Processes

- A detailed review process and protocol has been developed for the review of existing chemical processes. This review is primarily a reactive chemicals review but also includes process risk and loss prevention questions. The protocol and questionnaire is referred to as the RC/PHA (Reactive Chemicals/Process Hazard Analysis) review.


RC/PHA
Questionnaire

As can be seen from the *Global Reactive Chemicals Standard*, all existing chemical processes will have a Process Hazard Analysis/Reactive Chemicals review on a predefined periodic basis. In addition, every new plant Production Leader should review their process with the Reactive Chemicals Committee within 90 days of assuming responsibility for a pilot or production plant. Prior to the review, the Leader should acquire training on the chemistry and processes that they are working with. This should include an evaluation of raw materials, processes, products and waste to understand any potential reactive chemical hazards. They should review and be prepared to answer questions from the completed and updated RC/PHA protocol questionnaire as well as other relevant materials in their plant Process Safety Folder, such as F&EI, CEI, etc. The review should cover all auxiliary operations to the process such as: raw material and product storage; drum, tank car and truck loading.

- Changes within a facility are often made in processes which are considered small or minor but which could have major effects regarding potential reaction hazards. Hazards are often present in such changes as:
 - ♦ New supplier of raw materials and method of delivery
 - ♦ Equipment changes
 - ♦ Procedure changes
 - ♦ Changes in shutdown or startup plans or procedures
 - ♦ New computer control systems or program changes

These should all be addressed in the facility Management of Change process with the inclusion of adequate approval and review steps.


Guidelines for
Management of Change

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C. Support Operations

Many Dow operations are not directly connected with either the research laboratory or production plant. These may involve tank car and tank truck cleaning, bulk terminal operations, waste disposal facilities, power plants, etc. These and similar operations should undergo reactive chemical reviews similar to those of a production process described in B above.

D. Technical Service and Development

TS&D employees have a product stewardship responsibility for the products Dow manufactures and sells. As part of their stewardship activities they should obtain and communicate pertinent reactive chemicals hazard information to handlers and users of Dow products. They should also make sure that the MSDS sheets for their products reflect the current reactive chemicals test data.

E. Outplant and Contract Operations

The reactive chemicals review and hazard analysis processes should also be applied at contract and outplant operations where Dow has some responsibility for the operations or the technology of the facility. It may be necessary to consult with management and our attorneys in order to determine the responsibilities we have in reviewing the RC/PHA for the technology and operations in these facilities.

REACTIVE CHEMICALS TEAMS

A.1. Large Site or Location Team

The manager of a large division, site or location should establish a Reactive Chemicals Team consisting of qualified technical people. These teams will serve as a geographic multi-discipline resource for conducting the reviews. In cases where a plant or facility within the large site is aligned with a Technology Center that has a review process that adequately covers the Reactive Chemicals and Process Hazard Analysis issues, the RC/PHA review will be scheduled and led by the Technology Center. The Process Safety Services representative for the site will have a list of the Technology Centers that have "qualified" review processes. In cases where the facility has no Technology Center alignment, such as some research or site facilities, the review will be scheduled and administered by the Site Reactive Chemicals Review Team. In cases where the facility has a Technology Center, but the Technology Center Review Process has not been developed to the point of including and covering the RC/PHA issues, a formal understanding will exist between the Technology Center, the Site Reactive Chemicals Team and Process Safety Services on how the review needs will be covered.

When possible, the team should be composed of experienced representatives from Research, Engineering, Production, Process Safety, Testing or other appropriate functions. The responsibilities of the Large Site Reactive Chemicals Teams are to:

- Establish the program in a way that interfaces with the Technology Center process and within the framework of the *Guidelines for a Reactive Chemicals Program* and the *Global Reactive Chemicals Standard*.
- Provide the multi-disciplined and cross technology resources to participate in all reviews, including those scheduled and administered by the Technology Center. A key part of the Process Hazard Analysis/Reactive Chemicals review is the "outside in" evaluation that is provided by having reviewers that are outside the existing technology as part of the review team. This will require sharing of resource people between technologies and businesses. The Site Reactive Chemicals Teams are the means to provide this sharing.
- Provide data and consultation to owners and management concerning hazard evaluation of materials and processes.

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- Coordinate programs for hazard review of existing materials and processes outside the Technology Center Review responsibility.

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- Help investigate and report reactive chemicals incidents.
- Support the overall reactive chemicals effort by implementing ways to enhance awareness of reactive chemicals issues.
- Train people on reactive chemicals, using tools and resources provided by the centers of expertise. (This includes having access and utilizing the REACHEM database.)

It is recommended that one member of the team be designated chairman for administration of the program. It may be desirable for the team to establish a subcommittee or mini-committee so that process changes can be reviewed on very short notice without delaying the implementation of the desired change. Members of the site team will be responsible for preparing themselves prior to a review in an unfamiliar technology so that the review goes efficiently without a lot of basic training of the reviewers during the review.

A.2. *Small Site Reactive Chemicals Team/Focal Point*

The leader of a small site, location or organization should establish a Reactive Chemicals Team or Focal Points consisting of 1-3 people. These teams will serve as coordinators to make sure that all of the reactive chemicals needs are being provided for at all parts of the site. The process for conducting reviews will be different depending on whether or not the facility is aligned with a "Qualified" Technology Center (See Appendix A). In cases where the plant is aligned with a "Qualified" Technology Center that has a working review process that adequately covers the RC/PHA issues, the review will be scheduled and led by the Technology Center. The Process Safety Services representative for the site will have a list of the Technology Centers that have a "Qualified" review process. In cases where a facility at the site has no Technology Center alignment, the review will be scheduled and administered by the Site Reactive Chemicals Review Team utilizing the multi-disciplined reviewers provided, where necessary, by the large site Reactive Chemicals Teams (A.1 above). In cases where the facility has a Technology Center, but the Technology Center Review Process has not been developed to the point of fully including and covering the Reactive Chemicals and Process Hazard Analysis, a formal understanding will exist between the Technology Center, the Site Reactive Chemicals Team and Process Safety Services on how the review needs will be covered.

The Reactive Chemicals Team from the Technology Center and the Larger Sites (see A.1 above) will provide multi-disciplined review participants to support the reviews at the smaller sites. This is to be done in a way that does not create significant travel, i.e., utilizing phone and teleconferencing. The responsibilities of the Small Site Reactive Chemicals Team/Focal Point are to:

- Coordinate programs for hazard review of existing materials and processes outside the Technology Center Review responsibility for their site.
- Provide the oversight to make certain that all reviews are implemented and the facilities are in compliance with the *Global Reactive Chemicals Standard*.
- Help investigate and report reactive chemicals incidents.
- Support the overall reactive chemicals effort by implementing ways to enhance awareness of reactive chemicals issues at the site.
- Train people on reactive chemicals using tools and resources provided by the centers of expertise.

Note: Many of the responsibilities of the "Site Teams" will be changing during the transition to a more Technology Aligned Process. It is important that the Site Teams maintain a leadership role and not relinquish any responsibilities until there is a clear and agreed to transfer of leadership to the Technology Teams. It is anticipated that this transition will take several years.

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B. Technology Reactive Chemicals Teams

These are global teams that are focused on delivering reactive chemicals support for a specific technology. There are a number of support issues that these teams will work towards so as to "leverage" knowledge, data and operating discipline focused on preventing reactive chemicals accidents. The composition of these teams will typically consist of a Technology Center representative, a Process Safety focal point assigned to the technology and a Core Analytical focal point assigned to the technology. It may also include the Global Process Engineering Technology Leader if there are appropriate issues that this person can support. Examples of issues that might need Process Engineering support are relief valve sizing issues, chemical dispersion modeling or equipment design or scale up issues. The EH&S Business Operations Leader may also be part of the team, as appropriate. The deliverables and expectations of the Technology Reactive Chemicals Teams would be to:

- Standardize reactive chemicals worst case scenarios for the technology.
- Define appropriate reactive chemicals testing results and reactive chemicals analysis templates for the technology as it applies to the individual plants.
- Develop standardized interactivity/compatibility charts. (See Appendix D, Preparation of a Compatibility Chart)
- Integrate the Process Hazard Analysis/Reactive Chemicals Protocol into the Technology Center Review.
- Participate in reviews where appropriate. This should be done in a way that does not generate extra travel since in most cases the multi-disciplined resources will be provided by the Site Reactive Chemicals Committees (See A.1 above). (Teleconferencing or video conferencing can be used as an alternative to travel in cases where site multi-disciplined resources do not exist.)
- Review and monitor the status of PHA/RC Reviews across the technology and ensure that the recommendations were consistent across the technology.
- Monitor compliance with due dates and action items that come from the reviews.
- Be involved in reactive chemicals incident analysis and corrective actions globally.
- Actively work to implement the appropriate "Corporate Memory" as it relates to reactive chemicals events. This means having a strong focus on the elimination of repetitive reactive chemicals accidents.
- Lead the definition of the technology's MET (Most Effective Technology) so that it adequately addresses the preventive measures and lines of defense that need to be in place.
- Support the development of the Process Safety Folder for each facility in the technology.
- Lead the development of technology specific reactive chemicals training.

REACTIVE CHEMICALS REVIEWS

Reactive Chemicals reviews should be conducted on new processes, periodically on existing processes and facilities, on changes planned for existing processes and on changes in supervision. It is the owner's responsibility to arrange for these reviews with the local or Technology Center Reactive Chemicals Committee. The standardized Global RC/PHA protocol should be utilized for these reviews. Your Process Safety Services representative can help you obtain and use this protocol. (See B under "How to Apply Reactive Chemicals")

Guide for Preparation

- Review the process chemistry, including principal reactions and expected side reactions along with their *heat of reactions* and *pressure build up potential*.
- Review the reactive chemicals test data summaries for exotherms, shock sensitivity or other indicators of instability or energy release potential.
- Examine the chemical processes in detail while looking for possible uncontrolled conditions that might occur, including modes of failure, worst case scenarios and other ways of potentially having a reactive chemicals accident.

- Avoid reactive chemicals accidents by analyzing each phase of an operation from raw material receipts through product distribution for any point where a reactive chemicals accident could take place.
- Consider the consequences of not following procedures, i.e., incorrect order of addition or stoichiometry, no agitation, equipment failure, loss of power, reverse flow, deficiency or excess of catalyst, etc.
- Carefully review startup and shutdown procedures and the consequence of a time delay in any step of the process. Evaluate the consequences of an extended hold or shut down period on plant operation.
- Identify lines of defense which will be employed to avoid reactive chemicals accidents at each point.
- Complete or update the PHA/RC Questionnaire. If there is a Technology Center specific version of this contact, your Technology Center Reactive Chemicals representative for a copy. (For the non Technology specific version, see B under "How to Apply Reactive Chemicals.") It is essential that if there is a Technology Center specific version that the PHA/RC review portion be easily extractable so that it can be provided to regulatory agencies (if necessary) without providing the entire contents of the Technology Center Review.

Operations and management of an operation should use "worst case scenario" thinking in evaluating the process safety of the operation. At every point in the operation where an uncontrolled reaction might take place, there should be a review of the worst possible combination of conditions that realistically could occur. This may include such conditions as loss of cooling water, wrong combination of reactants, wrong position of valves, plugged lines, instrument failure, air leakage, loss of agitation, deadheaded pump, mishandled catalyst, etc. If additional, more in-depth analysis is needed, a HAZOP should be done. (References: *Process Risk Management Guidelines for Facilities and Distribution*; *Hazard and Operability Study Process*)


Process Risk
Management Guideline


Guidelines for
Hazard and Operability Stu

Once the worst case scenarios are identified, "lines of defense" should be identified or developed for each scenario. These lines of defense should be standardized across the technology, utilized as part of the training efforts and included in the operating discipline for the facility.

In addition, where appropriate the lines of defense should be tested and practiced on a regular basis to ensure the reliability of the systems. These tests should be documented as part of the facility records. Unreliability of protection systems must not be allowed to be a cause of an accident or allow an accident to result in more severe consequences.

REACTIVE CHEMICALS TESTING

One of the functions of Global Core Technologies R&D is the analytical discipline Reactive Chemicals/Thermal Analysis/Physical Properties (RC/TA/PP). Some of the capabilities of this discipline are testing and data interpretation for reactive chemicals hazard assessment. It is the responsibility of the owner of any chemical process to use this Dow resource to obtain the information which is necessary to design a safe and efficient operation. Information about the analytical RC Testing discipline including contact names can be obtained on the INTRANet at <http://dilbert.nam.dow.com/anasci/rctapp/rctapp.htm>.

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To provide basic reactive chemicals hazard data, the following thermal considerations and test guidelines have been developed. The descriptions of tests are necessarily brief and incomplete. The owner should, therefore, consult their Reactive Chemicals Testing partner for details of the test, its significance and limitations, and for a detailed interpretation of the test results.

The RC/TA/PP discipline can assist you to define safe and successful procedures when you have the following potential scenarios:

- energy release
- significant gas generation (e.g., by reaction)
- flammability problems (e.g., by reaction products)
- compatibility concerns for chemicals
- materials of construction reactivity concerns

A. THERMODYNAMIC CALCULATIONS

The potential energy that can be released by a chemical or chemical system can be calculated by means of computerized thermodynamic calculations. These calculations are based on knowing the end products or assuming the end products that might be expected. If the chemical or system has very little energy, any reaction is generally non-hazardous. However, if the reaction products are known or expected to be gaseous, a high pressure hazard is still possible (see Appendix B).

Thermodynamic calculations should be made early in a hazard evaluation. However, when assumptions are made regarding end products, the calculations should be backed up by other tests such as the DSC, mixing calorimetry and possibly ARC.

B. THERMAL STABILITY

The evaluation of thermal stability requires understanding the rate of such a reaction as a function of temperature and the heat generated per unit of material by the reaction. In many cases, if not most, information on the pressure increases during the reaction are also essential, particularly for vent sizing.

DSC scans are used for preliminary screening to determine whether an exotherm occurs and the approximate temperature and the heat generated. Because the temperature in these test devices is forced up at a fixed rate, the detected onset of reaction temperatures may be higher by 50 to 300 °C than the temperature where the heat release rate may affect a plant reactor or storage container.

Thermal data where reactions are detected at lower temperatures are obtained from test runs on an ARC or other more sensitive calorimeters. In the ARC, the temperature is raised stepwise and at a much slower effective rate than with the DSC. The ARC is nearly adiabatic and, thus, more nearly approaches plant reactor conditions. Another important advantage is the fact that the reaction pressure is monitored and recorded in the ARC.

- **DSC (Differential Scanning Calorimetry)**

DSC is a basic screening test and should be applied to all chemicals and mixtures unless the thermal stability has already been clearly established.

The sample (typically 1 mg) is sealed in a glass container (capillary or ampoule) in a nitrogen or air atmosphere. The reference material is typically an empty sealed container. The sample and reference are heated in an oven at a constant temperature rate (typically 10 °C per minute) from ambient to 400 °C. Energy flow to the sample is measured as a slight deviation in its local temperature. Data are

presented in terms of plot of heat flow vs. temperature. Processes (phase changes, reactions) total enthalpies are determined by integration of the heat rate curve.

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- **Mixing Calorimetry**

Mixing calorimetry screens the results of intentional or unintentional mixing for immediate heat or gas release. In the test (2-Drop calorimeter), ~ 0.050 ml of one reactant (solid or liquid) is added to a small (2 ml) glass vessel, equipped with a small magnetic stirbar. The vessel is sealed with a crimp on top with a sceptor and placed inside the calorimeter block. The second material (liquid or gas, 0.050 ml) is taken up in a gas-tight syringe and the syringe needle is mounted into the calorimeter, the needle piercing the sceptor. After thermal equilibration is achieved (~ 10-15 minutes), the experiment is started. An electrical calibration is carried out, followed by injection and mixing of the materials. The heat is recorded and integrated over a typical time period of 10-15 minutes (longer times possible). After the experiment, the sample is exposed to a gas buret through the sceptor via a transfer needle to check for any gas generation.

- **Macro-DTA (Differential Thermal Analysis)**

This instrument was designed to yield information intermediate between the ARC and the DSC. A sample of 0.2-0.5 g is loaded into a tube-like container and placed into the device (larger sample sizes may be used at slower scan rates). A thermocouple is connected to the outside of the tube and the cell is fitted with a pressure transducer. A similar, empty cell in the same oven with thermocouple serves as a thermal reference. The oven is heated at a slow, linear rate (0.5 to 1 °C/min), and the pressure and differential thermal data are collected. The data are presented in a fashion similar to DSC – Heat Rate (mW) vs. Temperature (°C). The thermal data are enthalpically calibrated by means of a series of standards (calibration at high heat rates may be non-linear). Detection of thermal events approaches the sensitivity of the ARC.

- **ARC (Accelerating Rate Calorimetry)**

This method determines the self-heating rate of a chemical under near-adiabatic conditions and will usually give a conservative estimate of the conditions for, and the consequences of, a runaway reaction.

The test is quantitative, but corrections must be made for thermal inertia of the sample container before the data can be applied to process systems. Activation energy, approximate heat of reaction, and approximate reaction order are parameters that can usually be determined. Pressure data obtained during an ARC run can sometimes provide information for vessel vent design.

- **Reaction Calorimetry**

A typical reaction calorimeter consists of a jacketed reactor, addition device, temperature transducer(s) and calibration heaters. There are a number of devices within Dow ranging from the commercially available Mettler RC-1 (1-2 L volume) to smaller, in-house reactors (10-50 ml). While each of these devices has their unique attributes (e.g., in-situ spectrometry, quick turn-around, ability to reflux, etc.), all of the calorimeters will produce a signal of heat flow vs. time. The heat flow is usually produced in response to the addition of a reagent or an increase in temperature. Volume of gas or pressure generated may also be measured.

- **VSP (Vent Sizing Package)**

The VSP is an adiabatic device used to study relief venting. The system uses approximately 80 ml of reactants and can be operated in three different modes. In the "closed" mode, the operation is similar to the ARC. Venting tests are performed with a predetermined upset condition. In the "top venting" mode, vent size and flow regime characterizations can be made without detailed knowledge of the kinetics or physical properties of the system. In addition, viscosity characterizations can be made by using the "bottom venting" technique. The major advantage of using the VSP for vent sizing

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purposes is the reduction in computational effort and uncertainty involved in interpreting ARC data. Use of stirring allows tests with heterogeneous materials. Similar to the ARC, VSP also allows "shot addition" of liquids.

C. SHOCK SENSITIVITY

Shock sensitivity data are necessary to evaluate the potential hazards in transporting and handling chemicals. Transportation here refers to both transporting materials through plant pipelines, valves, pumps, and to general transporting and handling when shipping materials from one location to another by rail or truck.

Shock sensitive materials react exothermally when subject to a pressure impulse. The impulse may come from a hammer-like blow, such as used in the standard drop-weight test, or a compression, such as might be experienced in a deadheaded plant compressor or valve slamming shut. Normally, shock sensitivity increases with an increase in temperature. Materials that do not show an exotherm on the DSC are seldom shock sensitive.

- **Drop-Weight Test**

This is used as a screening test and should be applied to any materials known, or suspected, to contain unstable atomic groupings (see Appendix C). The test measures the susceptibility of a chemical to decompose explosively when subjected to the impact produced by dropping a weight onto a small sample in a metal cup. Solids and liquids are tested under slightly different conditions; but, in both cases, the weight and/or height can be varied to give semi-quantitative results for impact energy. Results are not absolute, but can be used for comparing the instabilities of two or more chemicals under the conditions of the test. A negative result does not prove the absence of hazards, but does indicate stability, except under severe conditions.

- **Confinement Cap Test**

This test is used to determine detonability of a material using a blasting cap as an initiator. The blasting cap is ignited to set up a shockwave in the sample in less than 1 millisecond. If the material detonates, it will add energy to the system, which will split the aluminum tube in which it is confined. The amount of splitting is compared to known explosive materials. Tests may be run at elevated temperatures.

D. FLAMMABILITY

Flammability tests evaluate the hazard present when an ignition source is available. These tests range from the determination of flash point, flammable limits and autoignition to the very rapid and destructive burning in a dust explosion.

From the point of view of the potential for a fire, the closed cup flash point determination is usually the most important. In a perfect closed cup test, the vapor pressure is in equilibrium with the liquid at the temperature of the test. At the flash point, the vapor composition is at the lower flammable limit. In fact, the lower flammable limit can be estimated from vapor pressure data (for a pure compound). Open cup flash points are generally higher and, thus less conservative, than closed cup determinations. The value determined in an open cup test is subject to air movement at the open face of the cup and true vapor-liquid equilibrium probably does not occur.

Autoignition temperatures should be used with care. The surface area, the time of exposure to a given temperature, the availability of the oxygen supply and the ability of the system to lose heat will all affect the temperature at which a material self-ignites.

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A general rule for dust explosions is that any combustible material, if in fine particle form, can result in a dust explosion. The maximum pressures produced in a dust explosion are typically of the order of 100 psig. The rates of pressure rise and the ease of ignition, however, vary considerably from material to material.

- **Flash Point**

The flash point is the lowest temperature at which the vapors can be ignited under the conditions defined by the test apparatus and method. Flash points are necessary for safety considerations in a Reactive Chemical Review and are required by government agencies before registering and transporting chemicals. There are a number of standard methods:

- a. Tag Closed Cup (ASTM D56)
- b. Tag Open Cup (ASTM D1310)
- c. Pensky-Martens Closed Cup (ASTM D93)
- d. Cleveland Open Cup (ASTM D92)
- e. Setaflash Closed Tester (ASTM D3278)

For applicability and limitations of each test, consult the reactive chemicals testing supervisor or refer to the appropriate ASTM standards. In addition, ASTM E502 reviews the closed-cup methods and discusses potential problems with testing mixtures.

- **Flammable Limits**

Flammable limits, or flammable range, are the upper and lower concentrations (in volume percent) of a vapor in air which can just be ignited by an ignition source. Above the upper limit and below the lower limit, no ignition will occur. Data are normally reported for air at atmospheric pressure and at a specified temperature. Flammable limits may be reported for atmospheres other than air and at pressures other than atmospheric pressure.

The basic test apparatus consists of a chamber into which a known concentration of vapor (gas) in air is introduced. After thorough mixing, ignition is attempted with a spark or a hot wire. A series of different concentrations are tested to establish the upper and lower concentration limits for flammability. Although normally run with fuel-air mixtures at ambient conditions, other oxidizing atmospheres, diluent effects and temperature and pressure variations can be studied.

Flammable limits for most combustible gases and low-boiling liquids are known. Lower flammable limits can often be calculated reasonably accurately (see Appendix B), but calculations for upper flammable limits are less satisfactory.

If testing is required, the essential consideration is that the test temperature must be high enough to vaporize enough fuel. For the lower flammable limit, in air at atmospheric pressure, the minimum temperature is the closed-cup flash point. As a rough guide, the upper limit requires a temperature about 40 °C higher.

Tests on mixtures must be run at a temperature at which the sample is completely vaporized. If the vapor pressures of the components are widely different, results can be unreliable, and often cannot be related to the hazards under process conditions.

- **Autoignition Temperature**

The ignition temperature of a substance, whether solid, liquid or gaseous, is the minimum temperature required to initiate or cause self-sustained combustion, in air, with no other source of ignition.

Ignition temperatures observed under one set of conditions may be changed markedly by a change of conditions. For this reason, ignition temperatures should be looked upon only as approximations. Some of the variables known to affect ignition temperatures are percentage composition of the vapor or gas-air mixtures, shape and size of the space where ignition occurs and rate and duration of heating. Test results tend to be high and are *not* to be used for establishing "safe" temperatures. Under process conditions, there is a potential for fuel-air mixtures to ignite at much lower temperatures, due to extraneous sources of ignition that are virtually impossible to eliminate.

A special case of autoignition occurs for solids and liquids dispersed on high surface area solids exposed to air. Examples include used carbon beds, powdery solids and process fluids that have leaked on fibrous insulation. In all these cases, enough air can get to the solid to yield a significant rate of oxidation, but the heat loss provided through the bulk of the material is too low so that a thermal runaway occurs at temperatures lower than expected from the pure materials.

- **Dust Explosion**

Combustible, dusty material, with particle size less than approximately 200 mesh, can explode if a sufficient concentration in air is present along with an ignition source.

The screening test is used to determine the rates of pressure rise during an explosion, the maximum pressure reached, minimum dust concentration needed to support an explosion and the minimum energy needed to ignite the material.

A more recently developed 20 liter volume test device provides more reliable data for the design of vent and explosion relief.

E. INTERPRETATION

Every test has its own interpretation due to test limitation and variations in test conditions. Therefore, a person knowledgeable about the tests should be consulted, preferably before testing is requested, and again for interpretation of the test results. Consult with the local RC/TA/PP (Reactive Chemicals/ Thermal Analysis/Physical Properties) partner for help in interpreting the test data.

When applying the results of these tests to the plant environment, it is essential to recognize that these tests are conducted on a small sample under specified conditions that do not include all aspects of the chemical environment. Other important parameters are:

- a. Temperature-pressure variations
- b. Temperature-time variations
- c. Catalytic effects of contaminants
- d. Catalytic effects of container material
- e. Increased volume of system
- f. Stronger initiation energy than used in test
- g. Increased surface contact

Different environments exist in the laboratory, in the plant, in transportation, in storage, in field application and in disposal. These factors can be expected to have significant effect on the reactive properties of any material.

A large number of other tests and hazard evaluation techniques have been developed, both within Dow and by outside organizations. The owner of materials and processes should work with the local RC/TA/PP partner to determine what additional data are needed beyond those obtained from the basic screening tests.

DATA HANDLING

The owner of a material or process must obtain, maintain and update the reactive chemicals data necessary for safe operation. Data may be obtained from:

A. EXISTING DATA

- Technology Centers – The Technology Centers are maintaining files containing the reactive chemicals data pertaining to their plants.
- Computerized Database – Existing data generated at our various reactive chemicals testing laboratories is stored in a computerized database and is available to all employees. The database (REACHEM) is on the USRND VAX cluster. Information on the database may be obtained by calling (517) 636-0927.
- Literature – Reactive Chemicals data may be obtained for many materials from the technical literature and suppliers literature. (See the RC/TA/PP web page at <http://dilbert.nam.dow.com/anasci/rctapp/rctapp.htm>.)

B. NEW DATA

Data on new or unknown chemicals or mixtures may be obtained by submitting a sample to the reactive chemicals testing group in your area. It is very important to realize that every test has its own interpretation due to test limitations and variations in test conditions. Therefore, a person knowledgeable about the tests should be consulted for interpretation of the test results.

If an owner obtains new data from a reactive chemicals testing group or from a supplier, a copy should be forwarded to the appropriate Technology Center for its review and files. In addition, data generated on well-defined materials should be sent to CRI in Midland by the reactive chemicals testing groups.

APPENDIX A DEFINITIONS

Engineering Application – The engineering application of the reactive chemicals data that defines design parameters or operating conditions necessary to prevent reactive chemicals accidents.

Operation – The facility where the actual work is being done to manufacture, distribute, research or test chemicals.

Owner – A person who has defined responsibility for a proposal, a function, a work process, specific data or an idea. Use of the term "owner" needs to also clearly identify what is "owned" and what is the responsibility of that "ownership."

Qualified Technology Center – A Technology Center that has an established, functioning technology center review process that incorporates all of the key elements of Reactive Chemicals/Process Hazard Analysis in such a way that permits effective delivery of the review. The RC/PHA review must also be easily extractable from the Technology Center Review so that it can be provided (if necessary) to regulatory agencies without having to provide the entire Technology Center Review.

Reactive Chemicals Accident – An uncontrolled or unexpected chemical reaction that results in injury, property loss or environmental release.

(The distinction between *Accident* and *Incident* is important. Goals should be focused on the prevention of *Accidents*, and every effort should be focused on maximizing the reporting of *Incidents* and *Accidents* for improving awareness and learning. The premise here is that by vigorously working on the near miss *Incidents* we will be preventing *Accidents*. All reactive chemicals incidents, learning experiences and accidents will be reported so that the learning and awareness may be leveraged across the entire company.)

Reactive Chemicals Audit – The determination of the basic compliance of the owner with the requirements outlined in this standard.

Reactive Chemicals Incident – An uncontrolled or unexpected chemical reaction that has the potential for injury, property loss or environmental release. (A reactive chemicals "Learning Experience" is a type of incident where the potential for an uncontrolled chemical reaction may be quite remote.)

Reactive Chemicals Review – The consulting process that is focused on providing a reactive chemicals hazard assessment and recommendations for improvement.

Reactive Chemicals Testing – The fundamental testing done by analytical laboratories to evaluate the compatibility and reactivity of chemicals in a variety of processing and handling conditions.

Reactive Chemicals Worst Case Scenario – Plausible events within a facility that can result in an uncontrolled chemical reaction that has the potential to cause loss, injury or environmental harm.

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APPENDIX B

CALCULATIONS FOR CHEMICAL HAZARDS

Although some of these calculations can be done by hand, the capability for computerized calculations is available through Core R&D RC/TC/PP discipline.

Heats of Reaction, Combustion, Polymerization, and Decomposition

These are computed simply from stoichiometric coefficients and ΔH_f° for the reactants and products. Unknown ΔH_f° values can often be estimated with sufficient accuracy for rough applications by using methods such as:

- Group increments (see Stull, Westrum & Sinke)
- Benson's method, Chemical Review 69, 279 (1969)
- Handrick's ΔH_c method (Reid & Sherwood's book discusses this and other methods)

When ΔH_f° cannot be estimated satisfactorily, we try to estimate ΔH_f° directly by means of a similar "model" reaction which is known.

Equilibrium Composition (Conversion to Products) Prediction

This capability has many varied uses. It can direct research away from the blind alleys of infeasible reactions. It should be used more by those wanting to maximize production. Here is a yardstick by which to measure actual processes: Do they approach the predicted conversion to products? What are the effects of variables such as temperature, pressure and initial composition?

Our predictions are computed with a modified form of the chemical equilibrium program described by Cruise, *Journal of Physical Chemistry* 68, 3797 (1964). Gases, liquids, and solids are considered simultaneously. Calculations may be done isothermally or adiabatically. The method minimizes ΔG .

Reactive Hazard Prediction

The chemical equilibrium program is used in the adiabatic mode to calculate temperatures, heats and (crude) pressures for decomposition and oxidation. Stull (*Chemical Engineering Progress*, Loss Prevention, Vol. 4, p. 16, 1970) showed that these parameters are rough measures of *potential* reactive hazard.

Also available is the ASTM program, CHETAH, which is a program used for the estimation of explosive hazard.

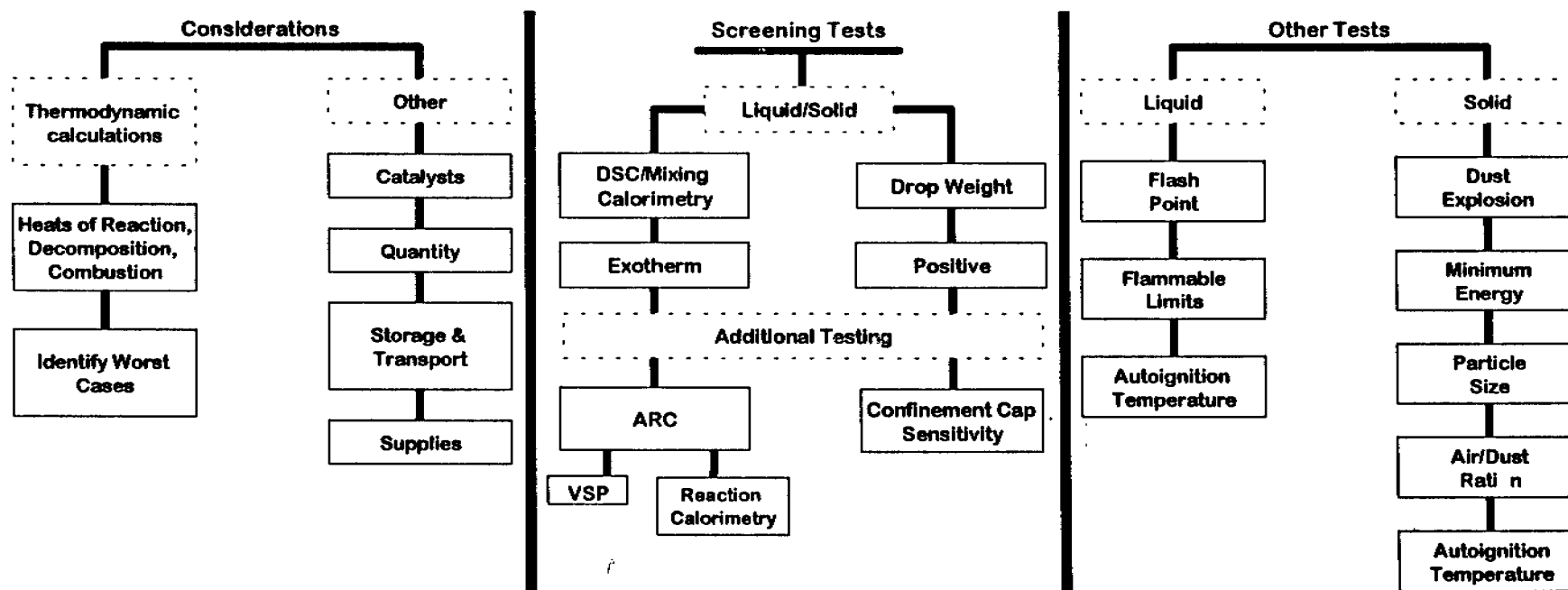
Flammability Limit Prediction

Lower flammability limits of vapors may be predicted quickly, including the effects of initial temperature and inert diluents such as N_2 and CO_2 . The limiting oxygen content necessary for flame propagation can also be predicted. The method applies to total pressures near atmospheric, to both pure and mixed fuels, and is not limited to oxygen as the oxidizer. When the fuel vapor-pressure curve is known, we can also predict flash points.

The chemical equilibrium program is used to calculate adiabatic flame temperatures as a function of volume percent of fuel. The predicted lower limit is the fuel percent corresponding to a threshold temperature. The same criterion sometimes yields rough values of the upper flammability limit, but there are complications in this fuel-rich region.

APPENDIX C CONSIDERATIONS AND TESTING DIAGRAMS

This outline is the owner's general guide for determining a potentially hazardous operation. Interpretation of results and need for additional testing should be determined in consultation with Analytical personnel and the Reactive Chemicals Committee.



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APPENDIX D

PREPARATION OF A COMPATIBILITY CHART

Preparation of a Compatibility Chart

The accurate assessment of binary chemical compatibility is an important part of the safe handling, transport and processing of industrial chemicals. The most common and convenient way to represent binary chemical incompatibility is through the use of a simple two dimensional chart or matrix. Binary compatibility charts are an extremely useful teaching tool for new and even veteran employees. Ideally, all components of interest (including common cleaning materials, water, heat, materials of construction, etc.) are listed on both the x and y axes of the grid and the intersection of the cells in the matrix represent the consequences of each mixed pair. Presentation of the data in chart form allows for quick use, especially in a process upset (i.e., emergency) condition.

Some general guidelines for preparation of a compatibility chart are given below. Much more detail may be found in the references below. Commonly available spreadsheet formats are amenable to the preparation of compatibility charts. Microsoft Excel, for example, may be used to set up such a chart quite conveniently. The chart may then be made accessible via a network server to all those involved in a common operation.

1. State the Scenario

By scenario we mean a detailed physical description of the process whereby a potential inadvertent combination of materials may occur. Details such as specific amounts of materials, temperatures, confinement (closed or open system) and the times the materials will be in contact contribute to the definition of compatibility.

2. Decide on a Hazard Rating Scheme

For example, a numerical score of 1, 2 and 3 might be appropriate with "1" indicative of a compatible mixture, a "2" might indicate a moderate hazard (e.g., a temperature increase) and a "3" might indicate a severe hazard.

3. Consider the Hazards for all Binary Combinations

The potential hazard for each binary mixture needs to be carefully considered. Avoid using blanks (empty cells) in compatibility charts since blanks may indicate that there is no hazard, or simply that the hazard is unknown.

4. Define the Categories

The definition of categories for the chart is an important part of construction. For small plants and operations, each chemical may be included in the chart and still be of manageable size. For more "general" compatibility charts the best manner to construct a chart is to group chemicals into natural groupings based on their chemical structure. Examples of these groupings are mineral acids, aliphatic amines, monomers, water-based formulations, halogenated hydrocarbons, etc.

5. Document How the Decisions are Made

Backup and supporting data should be easily accessible for chart users and for easy chart updates. If testing was performed to make a decision about a particular binary combination in a chart, then reference this test in the chart.

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More detail may be found in the following references;

A Review of Chemical Compatibility Issues

D. J. Frurip, T. C. Hofelich, The Dow Chemical Company, D. J. Leggett, Hazard Evaluation Laboratories Inc., J. J. Kurland, Union Carbide Corp., and J. K. Niemeier, Eli Lilly and Company, 1997 AIChE Loss Prevention Symposium, Houston.

Determination of Compatibility via Thermal Analysis and Mathematical Modeling

T. C. Hofelich, J. B. Powers, and D. J. Frurip, *Process Safety Progress*, vol. 13, No. 4, p. 227, Oct. 1994.

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