DEVELOPMENT OF ENHANCED CLASSIFICATION SYSTEM FOR OXIDIZERS

PHASE 2

1.0 PROJECT OBJECTIVE

The purpose of this research project is to develop a scientific and reliable method to classify chemical oxidizers based on the degree to which an oxidizer increases the burning rate of combustible materials with which it comes into contact. A test plan was developed to determine the property of and relationship between oxidizer chemical structure, composition, and packaging on the burning rate of oxidizers for classification and fire protection in storage environments. The resulting classification scheme for oxidizers is practical and includes a bench scale screening test method and medium scale burn testing of the oxidizer in its packaging with criteria for classification.

2.0 TEST PLAN OVERVIEW

The test plan for developing a classification system for oxidizers based on burning rate includes the following four elements:

- Oxidizer Selection Criteria
- Development of a Bench Scale, Screening Test Method
- Medium Scale Burn Testing
- Development of Classification Scheme With Performance Based Criteria

3.0 BACKGROUND

Oxidizers are defined, in part, as ‘materials that readily yield oxygen or other oxidizing gas’ that can increase the burning rate of typical combustible materials. Burning rate, or fire size, is best characterized by the energy released when a material is ignited or becomes involved in a fire. The energy released during active burning is characterized by the peak rate of heat release, time to peak rate of heat release and the total heat released. During decomposition and/or combustion, gaseous products are released and the initial mass of oxidizer and fuel is reduced accordingly. The peak rate of heat release typically corresponds well with the maximum mass loss rate during combustion.

Oxidizers, as a group of materials, may present multiple health and physical hazards. An oxidizer’s reactivity and potential for vigorous self-sustained decomposition when contaminated, exposed to incompatible materials or exposed to heat are included in the definition of an oxidizer in NFPA 400
Hazardous Materials Code\(^1\). The code’s Annex also includes chemical reactivity and thermal decomposition related hazards for storage conditions. Both the quantity and packaging (corrugated cartons, plastic buckets, supersacks, drums, tanks and bins) can influence the potential for contamination and toxicity issues as well as the level of protection required where these materials are used, handled and stored. Due to the number of variables associated with specific reactants, contaminants and environmental conditions and the influence of packaging, the test plan for classifying oxidizers will be based on the increase in ‘burning rate’ of typical combustible materials characterized by rate of heat release.

Phase 1 of the Development of an Enhanced Classification System for Oxidizers included a review of fire losses involving oxidizers and a review and evaluation of existing, potential and proposed test methods for characterizing oxidizers. A summary of key findings based on that review include the following:

- The current definitions for Class 1, 2, 3 and 4 oxidizers are subjective. Further, the oxidizers listed as typical of each Class in NFPA 400 Annex C are based on the technical committee’s evaluation of available data and the results of tests done by the Bureau of Mines and General Electric Research in the 1970’s. Recently, the list of oxidizers in Annex C was amended to include calcium hypochlorite formulated with magnesium sulfate heptahydrate.

- A majority of the large fire losses involved solid oxidizers.

- A bench scale test method that adequately correlates the ‘burning rate’ of oxidizers in different forms and packaging for large scale storage does not exist.

- The UN’s Recommendations on the Transport of Dangerous Goods bench scale test method (Test O.1) is used to assign packing groups to solid oxidizers for transportation. The test does not adequately reflect storage conditions or the influence of packaging or combustible materials other than cellulose powder. The determination of burning time is strongly dependent on test conditions, particle size and the test operator’s perception of the end of active burning. The UN Test O.1 is currently under review and revision by the Oxidizer Working Group of the International Group of Experts on the Explosion Risks of Unstable Substances (OECD-IGUS). Proposed revisions include gravimetric

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analysis during testing and using calcium peroxide\(^2\) as the reference oxidizer instead of potassium bromate.

- FM Global used the 50 kW Flammability Test Apparatus to collect rate of heat release and mass loss data for mixtures of oxidizers, cellulose and oxidizer-cellulose mixtures following the UN Test O.1 method to assign a packing group based on the measured data for the potassium bromate reference mixtures and select oxidizers\(^3\). A review of the data showed the rate of heat release, maximum mass loss rate and determination of active burning time based on mass loss were sensitive to differences in oxidizer:fuel concentrations and oxidizers from different classes.

- Rate of heat release data from large scale tests with pallets of empty packaging, packaging with inert material and packaged oxidizers showed the difference in burning rate of packaged trichlor (89% available chlorine) and calcium hypochlorite (>68% available chlorine) compared to empty packaging\(^4\). Included in the tests were corrugated cartons with Surlyn™ bags and HDPE bottles with granular and tablet form oxidizers. The rate of heat release data and visual observations were sufficient to re-class trichlor from Class 2 to Class 1. While the large scale burn tests most closely resemble oxidizers in storage conditions, the tests are cost prohibitive, not widely accessible and generate large amounts of waste.

- Medium scale (~ 60 lbs) free burn tests are useful in characterizing the burning rate of granular and tablet form oxidizers in their packaging. Rate of heat release based on gas temperature rise calorimetry, radiant heat flux and mass loss rate test data have shown a distinction in the enhancement of burning rate of packaged Class 1, Class 2 and Class 3 oxidizers compared to its packaging with and without an inert material. Granular salt was found to be a suitable inert material as a baseline material. Medium scale burn testing is not readily accessible but is less expensive per test than the large scale tests and generates less waste.

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\(^2\) 75 wt% calcium peroxide, 25% calcium carbonate.

\(^3\) Private communication with FM Global as part of Phase 1 Development of Enhanced Hazard Classification for Oxidizers.

4.0 TEST PLAN DETAILS

A block diagram showing the elements of the test plan is shown in Figure 1.

FIGURE 1. Block diagram showing overview of test plan for development of enhanced classification system for oxidizers.

A. OXIDIZER SELECTION CRITERIA

There are over 90 chemical oxidizers listed in NFPA 400 Hazardous Materials Code Annex C. A majority of the oxidizers are solids. A select group of oxidizers will be identified for inclusion in the test plan. The selection criteria for the oxidizers will be based on: 1) range of ‘burning rate’ based, but not exclusively, on current classification, 2) high volume in commerce and storage, and 3) willing contributions from oxidizer manufacturers. The necessary research and evaluation of current, historical, existing and available data will be done in order to select oxidizers with a range of burning behavior. Existing and historical test data will include results from DSC tests, BOM, GE Research, IMO,
Pot Test, UN Test O.1 results, SADT, etc. Fifteen (15) oxidizers are intended for inclusion in the test plan. A partial list of potential oxidizers include: sodium percarbonate, sodium carbonate peroxide, hydrogen peroxide, sodium chlorate and calcium peroxide.

Physical properties and test data for each of the selected oxidizers will be assembled into a spreadsheet with referenced source material. While not part of the test plan, a review of available DSC/DTA, ARC and other thermal analytical test data for the select oxidizers will be done. The Fire Protection Research Foundation will act as a depository for any confidential data provided by manufacturers. Before analysis and testing, the oxidizers will be further characterized for moisture content, activity assay and particle size distribution. The oxidizers will be stored in a cool, dry location.

Three fuels typically associated with oxidizer packaging and storage will be also subjected to testing and analysis. Typical combustible packaging materials include corrugated board, Surlyn™ thin film bags and high or low density polyolefin. Existing fire data from small, medium and large burn tests involving these fuels will be evaluated. The burning behavior, rate of heat release, mass loss and radiant heat flux from the combustible packaging materials will be measured with and without oxidizers.

B. DEVELOPMENT OF A BENCH SCALE, SCREENING TEST METHOD FOR OXIDIZERS

A bench scale, screening test method that does not require expensive test equipment will be developed and will generally model the UN Test O.1 conical test and the EU Test A.17. While under revision, the UN Test O.1 method for solid oxidizers is used to assign packing groups for transportation-- not storage. The conical pile test is a screening test used by the EU as a method for the determination of oxidizing properties. A meaningful bench scale screening test for the classification of oxidizers for storage will be developed using data collected from highly instrumented and well-designed tests with oxidizer-fuel mixtures with a 50 kW Flammability Test Apparatus. The fuels will consist of typical, combustible packaging materials.

The 50 kW Flammability Test Apparatus will be used with 30 gram samples of the select oxidizers in combination with different typical, combustible packaging materials. Ignition sources will include a Nichrome wire igniter and a needle flame. The 50 kW Flammability Test Apparatus will be modified to include two water-cooled heat flux gages, at fixed distances from the pile, and a thermocouple in the center of the pile. The test data will include rate of heat
release\textsuperscript{5} and mass loss profiles. The tests using the 50 kW Flammability Test Apparatus will include examining the influence of particle size distribution, ignition source, the influence of typical, combustible packaging materials and configuration, oxidizer concentration or dilution effects, and the need for or number of reference oxidizers.

The mass loss, rate of heat release, radiant heat flux and pile temperature data will then be evaluated and used to develop a bench scale, screening test method with 30 grams of the different typical, combustible packaging materials and select oxidizers that does not require expensive test equipment. A larger series of bench scale screening tests will be done for reproducibility/repeatability and evaluation of test parameters. Criteria for effectiveness as a screening test will include the test’s ability to distinguish between oxidizers with a range of burning behavior, product form and the interaction of oxidizers with different combustible fuels.

In the final classification scheme, the screening test method will be optional and manufacturers can opt to go to medium scale burn testing for classification. The screening test is necessary and useful for oxidizers, or formulated product, in development stages and to reduce the number and cost of medium scale testing for classification. The benefits of a meaningful bench scale test modeled after the UN Test O.1 method include: potential recognition and acceptance by UN, EU and GHS; low waste generated; low expense; and ability to execute without expensive test equipment.

C. MEDIUM SCALE BURN TESTING

Medium scale burn tests will be done to establish criteria for classification of packaged oxidizers based on the oxidizer’s contribution to increase or enhance the burning rate or rate of heat release of its combustible packaging when exposed to an external fire. There have been sufficient medium scale burn tests with oxidizers and formulated products packaged in corrugated cartons and HDPE pails to show this test method can distinguish the difference in burning rate of Class 1, Class 2 and Class 3 oxidizers in their intended packaging\textsuperscript{6}. The peak rate of heat release, time to peak rate of heat release, total heat released, mass loss rate and radiant heat flux of the packaged oxidizer will be compared with the burning behavior of typical packaging and typical packaging with inert material.

\textsuperscript{5} The rate of heat release measurements reported by FM Global were based on the energy associated with the formation of carbon dioxide in the combustion products released from the burning oxidizer and sawdust. Rate of heat release profiles based on gas temperature rise will also be generated from the 50 kW Flammability Test data.

\textsuperscript{6} During the research planning session, it was suggested the medium scale burn tests be done with different oxidizers in the same corrugated carton and Surlyn\textsuperscript{™} bag packaging.
Empty packaging, packaged salt and the packaged oxidizers will be centered on a protected table and load cell under a hood and instrumented exhaust collection duct and exposed to a 50 kW LP gas fire from a U-shaped burner. Generic corrugated cartons with Surlyn™ bags and generic HDPE pails, bottles or buckets will be used as representative of typical combustible packaging. During each test, the mass loss, radiant heat flux and gas temperature rise data will be recorded from ignition of the burner to the end of active burning or extinguishment. Two radiant heat flux gages will be located at a fixed distance from the packaging and packaged oxidizer. The combustion gas temperature data and hood constants will be used to calculate rate of heat release profile of the burner, empty packaging, packaging with salt and the packaged oxidizer. The increase in the burning rate of the combustible packaging, packaged inert and packaged oxidizer will be determined from the rate of heat release profiles including the peak rate of heat release, time to peak rate of heat release and total heat released. Mass loss rate and radiant heat flux data will be evaluated as providing additional data in the event of borderline cases.

A medium scale burn test with up to 60 lbs of packaged product typically requires less than 20 minutes. The proposed medium scale burn testing will include evaluating two typical packaging materials. The weight percent combustible material(s) per package will be determined before each test. Photographs and video cameras will be used to document the packaging and packaged oxidizers before, during and after each burn test. The remains after the burn test will be characterized.

A preliminary test plan for the medium scale burn tests include:

1) Propane burner (50kW fire) and hood calibration

2) Empty cartons with Surlyn™ bags
   a. 1 carton
   b. 2 cartons

3) Cartons with Surlyn™ bags each containing 1 lb granular salt
   a. 1 carton
   b. 2 cartons

4) Cartons with Surlyn™ bags each containing 1 lb granular oxidizer-inert mixtures (75:25; 50:50; 25:75) for three oxidizers.
   a. 1 carton
   b. 2 cartons

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7 The hood and instrumented exhaust collection duct are described in ISO 9705 Fire Tests-Full-Scale Room Test for Surface Products
5) Select Oxidizers  
   a. Cartons (2) with Surlyn™ bags each containing 1 lb granular select oxidizers  
   b. Cartons (2) with oxidizer in tablet and/or liquid form  

HDPE CONTAINERS  
6) Empty HDPE Containers  
   a. 1 container  
   b. 2 containers  
7) HDPE Containers with granular salt  
   a. 1 container  
   b. 2 containers  
8) HDPE Containers with select oxidizers  
   a. HDPE Containers (2) with granular oxidizers  
   b. HDPE Containers (2) with tablet oxidizer(s)  
   c. HDPE Containers (2) with liquid phase oxidizers  

As the test method for classifying oxidizers, a detailed description of the test instrumentation and set-up, calibration procedures, and calculations for rate of heat release will be provided.

D. DEVELOPMENT OF CLASSIFICATION SCHEME WITH TEST METHODS AND PERFORMANCE BASED CRITERIA  

The evaluation and testing of oxidizers and typical combustible packaging materials by the bench scale screening test will result in screening criteria. Oxidizer screening test criteria will include maximum mass loss rate and burning time determined by mass loss data. The results of medium scale burn testing of the select oxidizers in different typical, combustible packaging will be used to define the criteria for Class 1, 2, 3 and 4 oxidizers. The criteria for classification will include the peak rate of heat release and total heat released of the packaged oxidizer compared to its packaging. Time to peak rate of heat release, mass loss rate and radiant heat flux data will be evaluated for borderline classification. The test methods and the criteria for classification will be consistent with the existing levels of fire protection for the range of oxidizer burning behavior.

5.0 STATEMENT OF BENEFITS  

The benefits of developing an enhanced classification scheme for oxidizers include:  
- More scientific and less subjective classification for oxidizers in their intended packaging  
- Method to screen and evaluate oxidizers and formulated products
Eliminate the need for the technical committee to review and classify oxidizers for storage
• Potential for inclusion in Global Harmonization System for storage of oxidizers.

6.0 REPORTING AND DELIVERABLES

Due to the scope and magnitude of the test plan, the projected completion date is 18-20 months. Reports of results and progress will be done after the following milestones:

8 months:
1. Selection of oxidizers based on contributions and research of high volume commerce and storage chemicals.
2. Literature review and database of oxidizers subject to the test plan
3. Description of test conditions and results from 50 kW Flammability Tests
4. Report on progress

14 months:
5. Description of test conditions and results from medium scale burn testing
6. Report on progress

18 months:
7. Development of bench scale, screening tests to include different fuels and oxidizer:fuel mixtures
8. Description of test conditions and results of bench scale test
9. Report on progress
10. Defining Classes of oxidizers based on tests and data from select oxidizers
11. Development of Classification Scheme for Oxidizers with performance based criteria.

20 months
12. Preliminary Report for review and comments
13. Final Report and Classification Scheme

6.0 COST ASSOCIATED WITH TEST PLAN

The cost associated with executing the above test plan, final report and waste processing is $320,000.00. This amount can be reduced by the direct costs of chemicals and potentially through the collaboration with a laboratory.
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