CLASSIFYING AND CHARACTERIZING IN-PROCESS ENERGETIC MATERIAL USING LABORATORY AND SMALL-SCALE STANDARDIZED TESTS

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ABSTRACT

An approach is presented to classify and characterize energetic-bulk materials in manufacturing and/or demilitarization applications. This approach assists government and commercial manufacturers with proper facility design and siting of modified or new facilities. Understanding the characteristics of the in-process material ensures that proper safety requirements are addressed early in the designing and planning stages of a process. Established classification approaches for shipping and storage do not adequately address all of the issues associated with in-process operations and handling. However, standardized tests are available which allow for characterization of hazardous materials in operating scenarios.

1.0 Introduction

The United Nations (UN) has instituted criteria and test methods to determine an explosive material's shipping classification. In the USA, the Bureau of Alcohol, Tobacco and Firearms (BATF) has established criteria for determining whether an energetic material is considered a high or low explosive. Because the UN and BATF criteria were established for transportation and storage purposes respectively, they do not consider key elements that should be examined in a manufacturing situation. Currently, there is not a consistent standard available for explosive or energetic material characterizations and classifications applied to manufacturing or demilitarization operations. In the absence of a clear standard, UN and/or BATF classification systems have frequently been applied to these processes. However, an energetic material will typically provide the same or greater level of hazard in a processing operation than in a shipping or storage configuration. Therefore, the manufacturer or processor of explosive materials may be under assessing the hazard of the energetic materials in their processes by using the transportation and storage classifications as a guide.

Explosive classification of materials for shipping and storage operations has been found to provide greater safety to those operations through recognition and identification of the primary hazards associated with a particular material as packaged or stored. Standardized safeguards and regulations can then be applied to a variety of materials based on the determined classification. Emergency responders and others can be trained in the classification system and do not need to be intimately familiar with the materials in question to know basic precautions and procedures required. Laws and regulations based on these classifications have also been established. In-process classifications provide similar benefits to the manufacturer and/or regulator of explosives. Classified materials (process dependent) can be sited and safeguarded using basic procedures, standards and/or regulations based on the degree of hazard present. Consistent application of these in-process classifications for explosive materials will lead to greater safety in the workplace and a basis for continued improvement. Of course, a thorough hazard analysis of the process may reveal additional process specific hazards and requirements.

Some U. S. Department of Defense (DoD) and industry classification criteria have included classification and characterization tests applicable to in-process hazards from energetic materials. The UN, BATF and other classification systems, when used in combination with these additional tests can be used to produce an outline of recommended tests and criteria which can determine the hazard classification for in-process materials in manufacturing operations. Figure 1 is a decision tree for characterizing in-process bulk energetic materials. This flowchart was developed by incorporating the UN and BATF tests and/or criteria as well as additional tests used by the DoD and others in the explosives industry. Because the hazards from an in-process material may change at varying stages of processing, the classification methodology developed may need to be applied to each step in a process.

2.0 Explosive Classifications

In the USA, the UN tests and criteria for classifying hazardous materials have been adopted by the Department of Transportation (DOT) for commercial transportation classification and the by the DoD for military transportation classifications. Other classification systems are also used for explosives. The BATF has a separate classification system for explosives in storage applications. The Uniform Fire Code, Uniform Building Code (UFC/UBC) and similar state and local regulations or codes, typically regulate explosives using a combination of DOT/UN (transportation) and BATF (storage) classifications. The U. S. Department of Labor, Occupational Safety and Heath Administration (OSHA) requires determination of physical hazards in the work place, using appropriate scientific methods. However, OSHA does not specify the techniques to be used or classification terminology.

2.1 UN Tests and Criteria for the Transport of Dangerous Goods

The UN classification system for the transport of hazardous materials defines explosives as Class 1 materials. Explosives are also assigned a division number between 1and 6. The following table indicates the primary hazard of the material for each division number.

Table I. Primary Hazard Summary of the Divisions of Class I, Explosives

Class and Division	Hazards
1.1	Mass Detonating
1.2	Non-mass Detonating, Fragment Producing
1.3	Mass Fire
1.4	Moderate Fire, No Blast
1.5	Very Insensitive Substances w/ a Mass Explosion Hazard
1.6	Articles Containing Extremely Insensitive Detonating Substances (EIDS); without a Mass Explosion Hazard.

The UN test protocol evaluates new substances and new articles to establish whether they are explosive. The protocol classifies explosive substances in the packaged state for final designation in a hazard division within Class 1. Bulk material tests are also part of the protocol, but do not lead to a classification of the hazard presented by the unpackaged material.

2.2 Military Manufacturing Classifications (USA)

As stated, the DoD also uses the hazard classification system shown in Table I. "Primary Hazard Summary of the Divisions of Class I, Explosives". The recommended tests used by the DoD are essentially the same as those used by the UN to determine explosive characteristics[1]. The transportation classification is further identified as the basis for all storage, processing and handling operation classifications as well as for transportation[2].

However, the DoD recognizes that requirements for handling and manufacturing operations may need to be more stringent than for storage and transportation operations. As the DoD Contractors' Safety Manual states in regard to transportation hazard classifications: "However, such hazard classification information may not be valid when applied to the hazards associated with manufacturing or loading processes. For such processes, the materials and processes shall be analyzed on a case-by-case basis."[3] Similarly, the maximum amount of explosives permitted in any location is limited by the quantity-distance (Q-D) criteria, as it relates to the explosive classification. The DoD manual also states that: "distances required in the

[1] TB 700-2, Department of Defense Explosives Hazard Classification Procedures, January 1998.
[2] DoD 4145.26-M, Department of Defense Contractors' Safety Manual for Ammunition and Explosives, July 1987.
[3] Ibid.

standard Q-D tables may be reduced if structural data or engineering demonstrate that explosion effects will be reduced or eliminated through containment, direction or suppression shield, or building volume"[4].

What is not stated directly in the DoD manual, is that quantity-distances may need to be increased if the hazard classification of an unpackaged or in-process material is greater than for the packaged goods as classified for transportation. Also, evaluating every material in every process each time there is a process modification is very expensive. Proper characterization and classification of the in-process material, for appropriate states or stages found in the process, can lessen the expense and time required to properly analyze modifications to a process, or multiple processes and conditions.

2.3 BATF – Explosive Storage Classifications (USA)

The BATF defines explosives as any chemical compound, mixture, or device, the primary or common purpose of which is to function by explosion. The BATF classifies explosive materials into three categories for storage purposes. "High explosives", are explosive materials, which can be caused to detonate by means of a blasting cap when unconfined. "Low explosives", are explosive materials that can be caused to deflagrate when confined. "Blasting agents", are defined as any material or mixture, consisting of fuel and oxidizer, intended for blasting, not otherwise defined as an explosive[5]. Q-D requirements for magazine (explosive storage) separation and siting are based on these classifications.

The same concerns of propagation of an incident and harm to personnel, facilities and off-site concerns apply to a manufacturing environment. However, in a magazine, the only allowed operations are placing and removing materials. The range of hazards in a manufacturing operation is much larger, and much more complex. While the BATF criteria provide a guide, there are many process issues for which these criteria are not adequate by themselves to properly classify an energetic material. For example, a material may not be cap sensitive and would thereby be classified as a low explosive by the BATF. However, the critical diameter for propagation of a detonation may be only a few centimeters. In addition, the material may be able to transition to a detonation from a flame ignition under certain circumstances. In this example, a high explosive hazard exists for the operation, which must be recognized and addressed in order to maintain adequate safety in the operation and facility.

2.4 OSHA Regulation, 29 CFR 1910.109 and 1910.119 (USA)

OSHA Regulation 29 CFR 1910.109 defines explosives and blasting agents similar to the BATF except that OSHA includes: "The term "explosives" shall include all materials which are classified as … explosives by the U.S. Department of Transportation"[6]. To determine the physical hazards of a mixture that has not been tested "the manufacturer, importer, or employer may use whatever scientifically valid data is available to evaluate the physical hazard potential of the mixture."[7]

In the USA, this OSHA requirement, combined with the process safety standard found in 29 CFR 1910.119, manufacturers of explosives are required to assess the hazards associated with each explosive operation. However, frequently those performing the analysis are not familiar with the range of characterization testing and data available and rely on limited information or transportation and storage classifications of in-coming or finished products for these analyses. While an established in-process classification protocol will not resolve all issues that should be addressed in a hazard analysis, it does provide a basic set of criteria and data. This then helps to direct the analyst and provides a basis for occupancy and exposure guidelines, Q-D tables and other requirements, based on the classification of the material and applicable standards or regulations.

Officials for regulatory agencies may have minimal direct explosives experience. An accepted scheme for classification of explosives in the manufacturing environment provides them with the tools to consistently

[4] Ibid.
[5] ATF P 5400.7, ATF-Explosives Law and Regulations, June 1990
[6] 29 CFR 1910.109, "Explosions and Blasting Agents", August 1992
[7] 29 CFR 1910.1200, "Hazard Communication", August 1992.

and more confidently assess facility siting, building and fire protection plans, and related requirements prior to issuing a permit.

2.5 UFC and UBC Classifications (USA)

The UFC and UBC (and other civilian codes commonly used in the USA), currently define explosives in a similar way as the BATF, using the terms high explosives, low explosives and blasting agents. The UFC also references the DOT/UN (transportation) classifications. These classifications are tied to Q-D tables and recommendations or requirements for siting, building occupancy, fire issues, etc. However, the code official and the manufacturer of energetic materials are left without a clear path for implementation. This often results in uneven handling of issues across jurisdictions and even within the same jurisdiction. In such an environment, safety issues may be overlooked while economic burdens are increased without the desired benefit being fully achieved.

3.0 Bulk Energetic Materials Classification Decision Tree for Manufacturing Applications

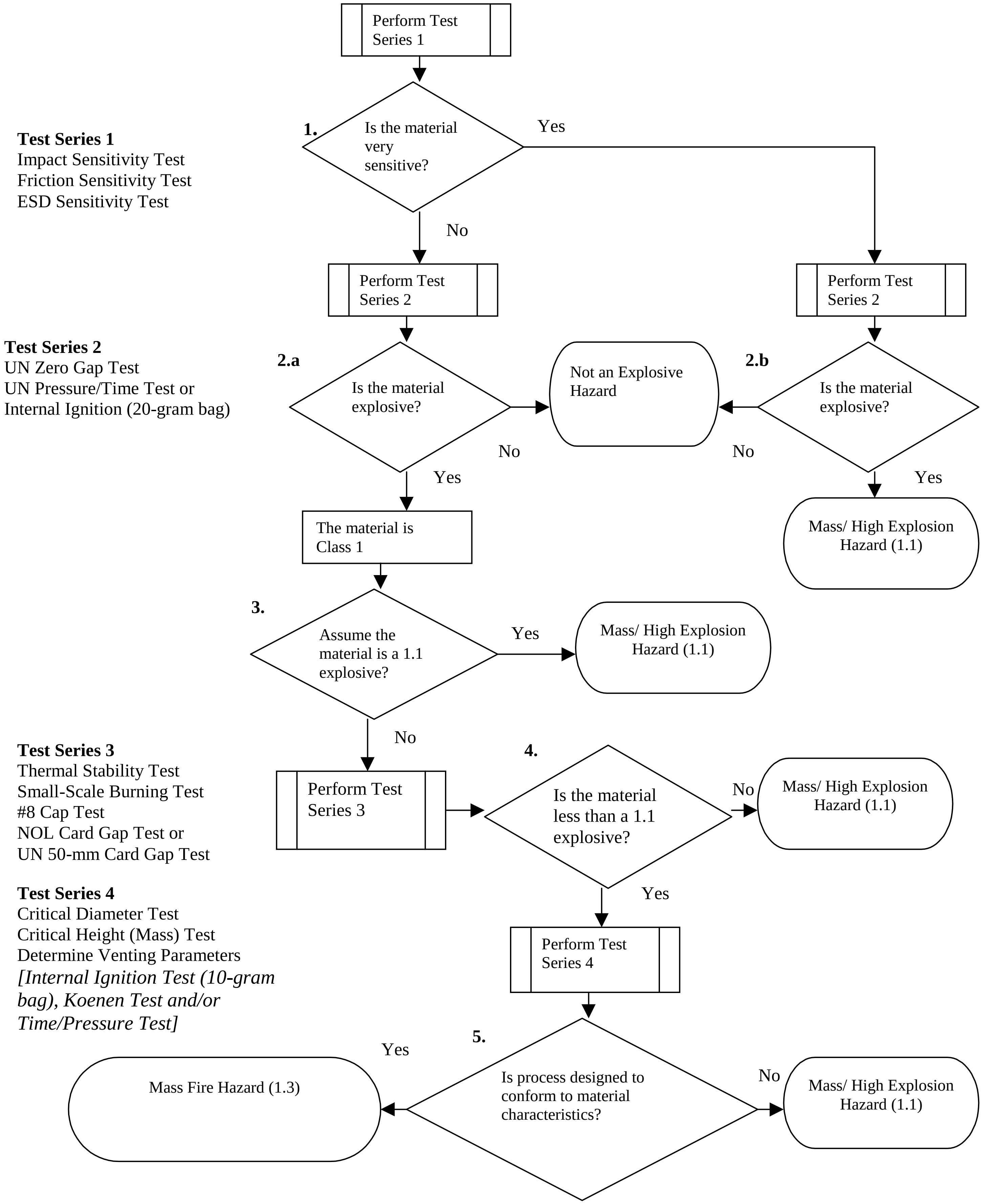
The decision tree in Figure 1, for characterizing energetic materials in a manufacturing or demilitarization operation, was developed by incorporating the UN and BATF tests and/or criteria and other standards. Since the BATF and UN have well defined classification systems, these classification schemes are incorporated into the decision tree where they apply. However, since the UN and BATF were established for transportation and shipping purposes respectively, they do not consider key elements that should be examined in a manufacturing or demil situation. Tests accepted as industry standards are included which address these key factors. Additional DoD classification criteria have also been incorporated into the decision tree where applicable. The in-process classification terminology used is the same as that adopted by the UN, as shown in table 1, above. While the decision tree and text presented is designed to address explosive materials in bulk, that is, in a non-packaged nor containerized form, explosive articles can be addressed using modified versions of the UN tests for 1.4 and 1.6 articles.

3.1 Test Series 1, Material Sensitivity

As shown in Figure 1, below, Test Series 1 consists of tests that determine material characteristics fundamental in determining processing and handling hazards. Friction, impact and ESD tests are specified. These tests have been placed first because impact, friction and ESD sensitivity data must be obtained on materials suspected of having energetic properties <u>prior</u> to handling them in the larger quantities required for the remaining test series. Other tests may also be appropriate prior to performing larger scale tests. For example, thermal sensitivity tests such as auto- ignition, and/or compatibility tests may also be conducted on the material. However, for purposes of classifying in-process energetic materials, as a minimum, these three fundamental handling tests are required before proceeding.

There are different techniques and degrees of investigation used when performing material sensitivity tests. The UN tends to require screening tests, which provide a simple pass/fail criteria. The impact and friction screening tests used by the UN protocol are also adequate for in-process classification. The ESD test is best done with an approaching needle apparatus, as this better simulates the hazard being investigated. If a material is found to be very sensitive in any of these tests it is considered a division 1.1 explosive for manufacturing if it also has explosive reactivity as determined in test series 2.

Figure 1. Energetic Materials Classification Decision Tree for In-Process Operations



3.2 Test Series 2, Material Reactivity

The UN includes the zero-gap test and, the time/pressure test or internal ignition test using a 20-gram bag igniter in the series of tests to determine whether a material is an explosive. The zero-gap test determines whether the material can propagate a detonation. The internal ignition test determines if the test material, when ignited, will deflagrate explosively or detonate under high confinement. Similarly, the time/pressure test determines if ignition will lead to a deflagration with explosive violence.

If the material has either of these explosive characteristics, it should be classified as an explosive in a manufacturing operation. If the material is shown not to have these explosive characteristics and is not manufactured for producing a practical explosive or pyrotechnic effect then the material is not classified as an explosive. However, the material may still exhibit explosive reactions under extreme or rare circumstances.

If Test Series 1 identified the material as a forbidden substance according to the UN or if the material was found to be extremely ESD sensitive, and Test Series 2 identified the material as an explosive material, the material would be considered as a 1.1 for manufacturing applications.

3.3 Test Series 3, Mass Explosion Hazard: High Versus Low Explosive

Test Series 3 is a compilation of tests to determine whether or not the material should be considered to have a mass explosion hazard. That is, is the material a Division 1.1 explosive or may the material be eligible for a lower explosive category (e.g. Division 1.3 or 1.5). The test series contains four different tests: the thermal stability test, the small-scale burning test, the #8 cap test and the UN 50-mm card gap test or NOL card gap test.

The UN includes the thermal stability test and the small-scale burning test in the test series which determines whether a material is forbidden for transport. If the material cannot pass both of these two UN tests, it is not allowed to be shipped in the tested form. In a manufacturing situation, where materials are being processed, handled and manipulated, materials which fail these tests should be considered to pose a mass explosion hazard.

The BATF uses cap sensitiveness to distinguish between high and low explosives for storage purposes. The #8 cap test as used by the UN is a good test to determine this characteristic. If the material fails the #8 cap test, then the BATF specifies a high explosion table for storage siting. In the past, the DoD used the #8 cap test as one of the tests to distinguish between a 1.1 and 1.3 material in bulk form[8]. In manufacturing operations, a cap sensitive material should be considered to have a mass explosion hazard.

The UN uses the UN 50-mm gap test to decide if a material is too insensitive to classify as an explosive for transportation purposes. For manufacturing conditions, a material which has been shown to be an explosive (series 2) should not be excluded. However, a material, which is very insensitive to shock and passes the other tests in this series, does not present an eminent mass explosion hazard. Therefore, the DoD has used the NOL card gap test as one of the tests to distinguish whether an explosive material is a 1.1 or a 1.3[9] while in bulk form. In accordance with DoD practice, the protocol in figure 1, recognizes that an explosive material should be considered as a mass explosive (Division 1.1) in manufacturing situations, unless it is sufficiently insensitive to pass this test (and the other tests in this series).

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[8] TB 700-2, Department of Defense Explosives Hazard Classification Procedures, December 1989.
[9] Ibid.

3.4 Test Series 4, Material Characteristics and Process Configuration

Test Series 4 includes tests to determine some material characteristics not included in the UN or BATF protocols. The tests listed are tests used by the DoD or members of the explosives industry. They help to determine material characteristics which, in turn, are used to define process parameters. If the process is designed within these parameters, the maximum credible event from the material or process is a mass fire hazard. This test series includes a critical diameter test, a critical height (or mass) test. The series also includes tests to determine venting parameters, for confined operations.

Critical diameter refers to the minimum diameter a quantity of an energetic material requires in order to propagate a detonation. Critical height refers to the degree of self-confinement provided by a pile (in a steel pipe) of the energetic material. The critical height tests, determines the material height as a function of pile diameter at which a low rate reaction (flame initiation event) transits to a higher order explosive reaction (explosion or detonation). The critical diameter and critical height are used to determine basic process parameters such as process vessel and transfer line dimensions.

The Internal Ignition Test (10-Gram Bag) is similar to the internal ignition test in series 2, except that a 10-gram bag igniter is used instead of the 20-gram bag. The test determines if a material will explode or detonate when initiated with a mild source under confinement, as may occur in a manufacturing environment.

The Koenen Test and Time/Pressure test are used by the UN transportation tests protocol to determine the reactivity of a material to intense heat under vented confinement and to the rise in pressure due to confined burning, respectively. These tests can also be used to evaluate the degree of venting or other relief required to avoid an explosion in the process.

4.0 Summary and Conclusions

The DOT/UN, DoD, BATF, OSHA, UFC, UBC, and others have regulations concerning explosive materials. In each regulation, the explosive materials are defined, categorized and classified according to the purposes of the regulation. Since there has not been a classification system established for manufacturing operations, the UN and BATF classification systems for transportation and storage, respectively, have often been applied to materials in manufacturing processes.

However, because the UN and BATF were not established for processing applications, they do not investigate certain material characteristics which should be examined in a manufacturing situation. Furthermore, it is reasonable to expect that a bulk energetic material may have a greater level of hazard in a manufacturing operation than in an established shipping or storage configuration.

Figure 1 is a decision tree for characterizing energetic materials in manufacturing operations. Since the BATF and UN have well known and well defined classification systems, the tests and/or criteria established by them were incorporated into the decision tree where they could be applied. Additional tests have been included which investigate material characteristics beyond the charter of the UN and BATF protocols, but which are meaningful when applied to manufacturing configurations.

The decision tree assists the user in classifying bulk energetic materials at various stages of manufacture. This can help to establish the correct material and personnel limits for the process, facility siting and other code issues, in addition to maintaining the proper understanding of the material's behavior.

Not-withstanding the assistance provided by the decision tree, specific hazards, which are identified by conducting hazards analyses on the process, may require further analysis of the materials involved to ensure safe operations.