



UN test O.1 errors in quantifying the behavior of solid oxidizers



Vytenis Babrauskas

Fire Science and Technology Inc., San Diego, CA 92103, USA

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ABSTRACT

The results of the UN test O.1 for oxidizing solids are shown to be incorrect when specimens contain certain inertant additives, illustrated for the case of oxidizers in the ammonium nitrate fertilizer family. Test results for three different AN-based products containing inertants show that two of the three (including calcium ammonium nitrate, CAN, a long-known safer alternative to AN) would be misranked with the O.1 test. An analogy between the heat release rate of substances containing fire retardant (FR) chemicals is established and several ways by which FR behavior can be achieved are demonstrated. It is shown that the O.1 test implicitly adopts only one model of inertant action, and that chemicals which rely on a differing mode of inertant action are liable to be incorrectly treated. It is further shown that the physical basis of the O.1 test—an intimate mixture of finely-comminuted fuel and oxidizer—misrepresents the most common type of accidents involving oxidizers, and that such test results do not correspond to scenarios of a less extreme nature. The new O.3 test improves the analysis method, but does not resolve the problem of excessive commingling of fuel into oxidizer. It is recommended that the intermediate-scale arrangement used by the Bureau of Explosives be adopted for further development and standardization, in preference to the O.1 or O.3 test arrangements.

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1. Introduction

The only standardized test currently used for oxidizer chemicals is Test O.1 (Anon, 2009) in the UN Manual of Tests and Criteria (apart from the new O.3 test, discussed later). The O.1 test is intended to assess the oxidizing propensity of materials in order for them to be classified into Packing Groups for transportation regulation purposes. It forms the basis for national regulations in essentially all countries. Apart from the description in the UN book, little research or background for this method has been published. Oxidizing solids, in general, have received very little attention. The former Bureau of Mines (BM) conducted the earliest study (Kuchta et al., 1972) focused on developing a test method, while researchers at General Electric (King and Lasseigne, 1972; Hough et al., 1973) expanded and elaborated on the BM work. Those studies, while valuable, are not relevant to the O.1 test, since these workers only used a physical arrangement which was dissimilar to the one eventually adopted by UN. Later, as the UN group had already started its work, Japanese researchers (Uehara and Nakajima, 1985) published a study which, again, was based on a test arrangement dissimilar to the O.1 test. The O.1 test itself is

understood to have been evolved by a UN working group which did not publish any documentation on its development work. Subsequent to the test being finalized, the only published research have been papers by Hasegawa et al. (1989) and Koseki and coworkers (Koseki, 2001; Koseki et al., 2001; Koseki et al., 2002). These papers delve into several standardization issues which are not directly related to the present study.

The UN O.1 test involves 30 g of material where the test oxidizer and the cellulose powder and uniformly mixed together, poured into a 70-mm, 60° glass funnel, and inverted into a conical heap on a noncombustible substrate board. A Nichrome wire heater bent into a loop sits near the bottom of the pile. The test entails igniting the fuel/oxidizer mixture by heating the wire to approximately 1000 °C. There is only one criterion for judging the results of the O.1 test and that is duration of flaming. Longer duration of burning is assumed to denote lesser hazard due to oxidizer action. For actual classification of chemicals, comparison is made between the test results and a reference oxidizer. In addition, two variants of test have to be run, with 1: 1 and 4: 1 ratios of oxidizer: cellulose.

The present study was motivated by a concern over very serious accidents where ammonium nitrate (AN) fertilizer is involved and a fire leads to detonation with disastrous consequences (Babrauskas, 2003; Marlair and Kordek, 2005; Babrauskas, 2016). AN is classified in the UN system as a Division 5.1 PG III solid oxidizer. Adoption of

E-mail address: vytob@doctorfire.com.

safer alternative fertilizer materials which are less active as oxidizers would reduce the potential for such accidents.

2. Methods and materials

Since the purpose of the study was to examine the relative oxidizer performance of various materials and not to achieve a UN classification, a simplified version of the O.1 test was conducted. Only the 4: 1 mixture of oxidizer: cellulose was tested. Potassium bromate (which is a suspected carcinogen and may have to be substituted by UN) was not utilized. Temperature in the laboratory was 22 °C and relative humidity approximately 35%. Video recordings of all tests were made and the analysis, discussed in a subsequent section, relied on these video records.

Four materials were tested for oxidizing potential: AN (Amtrate, produced by CF Industries and supplied by Armstrong Forensic Laboratory), calcium ammonium nitrate (CAN, produced by Yara as CAN-27 and supplied by J.R. Simplot Co.), Ferti-Safe (FS, comprising AN coated with calcium sulfate [at a 20% loading level] derived from fly ash, supplied by Darrell Taulbee, Univ. of Kentucky), and Honeywell Sulf-N 26 (SN26, now produced by J.R. Simplot Co. as ASN-26). Chemical characterizations of AN (Kiiski, 2009), CAN (Zapp et al., 2005; Anon, 1964, 2000), FS (Taulbee et al., 2009), and SN26 (Kweeder and Iwamoto, 2007; Stevens et al., 2010; Kweeder and Williams, 2011; Kweeder and Wissinger, 2012; Levy et al., 2014) have been published.

All materials were visually examined prior to testing. All were in the form of prills, roughly 2 mm in diameter. None of the specimens showed any degradation or deterioration, i.e., all were comprised on integral prills without clumping, dusting, or foreign matter. The color of AN prills was white, CAN gray, FS light yellow, and SN26 white. Since the O.1 test suggests that friable materials be powdered in preparation for the test, the test materials were powdered with an electric grinder until a uniform texture was achieved.

The preferred cellulose for running O.1 tests had been Whatman CF-11 cellulose powder. This was discontinued by the manufacturer, and European laboratories adopted Technocel 75 as a replacement. However, this product is not available in North America. Consequently, several different cellulose powders were explored and Microcrystalline Cellulose Powder, from MP Bio-medicals was adopted. Ignition was accomplished by a 300 mm long, 22-gauge Nichrome wire heated up to approximately 1000 °C. The wire was bent into the shape as illustrated in the UN Manual. A new Nichrome wire was used for each run. Each test started by turning on the power to the heater, and terminated when no more combustion was seen to be occurring.

3. Preliminary analysis of results

Preliminary analysis of results indicated that CAN would be classified as a more potent oxidizer than straight AN by the O.1 test criteria, since its flaming ceases in about half the time that it takes flames to go out with AN (see the last number in the last column in Table 2). This conclusion would, in fact, be the exact opposite of its actual behavior, as it is known (Babrauskas, 2016) and is presented

later. In the UN system, the tests described are to be used only for novel materials. But many materials are classified prescriptively in the system, and for such materials the prescribed classification governs (Anon, 2013). Without recourse to testing, AN is classified as a Division 5.1 oxidizer, while CAN is not only not a Division 5.1 oxidizer, but it is not ‘dangerous goods’ of any division (Anon, 2006). This is consistent with the fact that numerous AN storage or transport disasters have been documented, but none that would involve CAN (Anon, 2014; Babrauskas, 2003, 2016; Marlair and Kordek, 2005).

This test finding required investigating to determine if the test can yield variables which do have a credible correlation to the known behavior of the material. In the tests conducted here, it was found that some specimens exhibited a tendency to shoot out jets of flame (Fig. 1), often in a near-horizontal direction. This will be referred to as *flame jetting* here. Additionally, some specimens showed *sparkler jetting*, where a shower of very bright, incandescent particles is shot out, often in a lateral or oblique direction (Fig. 2). Ordinary fuels burned in air (Fig. 3) do not show sparkler jetting, which is a trait of small particles of fuel intimately combined with solid-phase oxidizer, such as seen with pyrotechnics. Again, this was interpreted as a mechanism whereby spreading of fire laterally may be promoted.

In analyzing the videos of the test results, “flaming” was taken to mean distinct visible flames that can clearly be differentiated from surface glowing or smoking. In normal gravity, unobstructed flames are buoyant and move upwards in a vertical path. “Flame jetting” was taken to occur where jets of flame were seen issuing that were clearly not conventional, upward-buoyant flames. “Sparkler jetting” was taken to occur where a shower of bright, incandescent particles was being discharged with a visibly strong velocity. Many tests also produced some ejected embers that were evidently of lower temperature (orange, not white) and did not correspond to a localized jet being ejected. Such embers were not included in the tabulation of results since means were not available for quantifying this behavior, nor were small, low-temperatures particulates necessarily indicative of fire spread hazard.

4. Action of FR additives

The mode of action in the O.1 test for inertants added to AN have not been examined in prior research, and the present study is the first on this topic. However, the action of FR additives on combustible materials, most typically plastics, has been studied for decades. The hazard variable most commonly measured in such research is the heat release rate (HRR) (Babrauskas and Grayson, 1992). This can be a valuable engineering property, since by use of oxygen consumption calorimetry it can be accurately measured and reported in units of HRR/specimen area, i.e., kW m⁻². HRR is considered to be the single most important hazard parameter describing a fire (Babrauskas and Peacock, 1992).

In the course of research on FR additives on the HRR of materials, it has been found that the most common effect is to decrease the peak HRR while at the same time prolonging the time of burning (Papaspriides and Kiliaris, 2014), see FR “A” in Fig. 4. This mode of behavior is exactly the implicit assumption of data analysis

Table 1
Summary of test results obtained.

Material	Average flame jetting duration (s)	Average sparkler jetting duration (s)	Overall flaming duration, average (s)
AN	106	99	163
CAN	10.3	0	56
FS	6.1	0	45
SN26	0	0.17	435

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