

The Saga of ASTM Standard G 124:

*How a Standard Intended to
Make Oxygen Systems Safe
Became Unfit for Use*

Barry L. Werley

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Introduction to The Saga of ASTM Standard G 124

REFERENCE: Werley, B. L., “Introduction to: *The Saga of ASTM Standard G 124*”, *The Saga of ASTM Standard G124 (2010 and 2018 Versions); How a Standard Intended to Make Oxygen Systems Safe Became Unfit for Use*”, Self-published public domain opinion, 2020, p. 5-8.

ABSTRACT: From 1992 through 2019 the writer defended historical approaches to the measurement and application of fire-limit data for the prevention of unseemly accidents. During the time, key members of ASTM Committee G4 supported and ultimately deployed an approach (2010) that differs significantly and is based on a short burn criterion to define self-sustaining combustion. *The Saga of ASTM Standard G 124* compiles the writer’s sequence of analyses that ultimately lead him to declare G 124 has become unfit for use.

KEY WORDS: oxygen, ATM G 124, combustion, behavior, metals.

ASTM Committee G-4 was formed in 1975 and through 2010 its standards have reflected historical approaches to fire-accident control. However, when its first metal fire-limit test procedure, ASTM G 124-1994 on *Determining the Combustion Behavior of Metallic Materials In Oxygen-Enriched Atmospheres* was pursued, there was a contingent that sought to define a positive burn with a small amount of combustion rather than with traditional methods that seek equilibrium or greater combustion and use long amounts of combustion, often complete specimen combustion to indicate a positive burn. In the early 1990s the G-4 Committee agreed to tradition and adopted roughly complete combustion of six-inch long specimens as the indicator of the threshold.

However over time, the short-burn contingent including key members repeatedly sought adoption of a short criterion with numerous ballots of a revised draft. The writer cast negative ballots every time. Curiously, instead of a normal negative-ballot reconciliation process, each time the ballots were withdrawn and though other negative votes and comments were often reconciled, the burn criterion debate was in effect censored.

A short criterion would greatly simplify testing and reduce the cost, but a technical bases to justify the change was never presented formally nor were the technical bases that dispute such a change challenged leading the writer to presume the change was being pursued as intuitively obvious, a possibility he himself had once contemplated.

In one of these ballots in 2002, the writer, wearying of casting long technical nega-

¹No mailing address. This paper and book are being archived as public domain, public service opinion expected to outlive the author.

²Italic numbers in brackets refer to the reference list at the end of the paper.

tive arguments prepared a separate detailed [1]² analysis for the Committee. He would simply cite it in any future negative ballots.

In 2009, a paper on a test program at the NASA White Sands Test Facility [2], alleged to have measured a valid burn criterion of 1.18-inches (30-mm) and a ballot of a short-criterion draft G 124 standard was issued later that same year. The writer cast his traditional negative, citing his analysis, and for the first time the negative was challenged.

The NASA work was proffered to the writer as proof of the short criterion. The writer's argument [1] and historical context in his negatives were not considered at all. However the writer promptly cited what he considered to be at least two disqualifying flaws in the supportive paper [2]: (1) the paper's assertion that an igniter's influence ends when a first droplet of slag falls away citing igniter materials that had been observed to be retained in the residual melt, and (2) that the new procedure conflicted with G-4's *Standard G 125 on Measuring Liquid and Solid Material Fire Limits in Gaseous Oxidants* (for Oxygen Index testing) which cited interpretation guidance for similar testing. The persuasiveness of the negative was thereby decided not on its *own* merit but on whether the writer's cited flaws in the NASA work were convincing. The first alleged flaw cited was rejected on the basis that the cited data had apparently not been published, and the second because the attending members disavowed knowledge of how to apply the guidance of G 125 to G 124. Only five subcommittee members were present for the crucial vote and only ten Main committee members for the subsequent vote. The negative was found non-persuasive and G 124-10 became adopted.

In the early days of Committee G-4's existence the lore of the "full consensus" nature of ASTM Standards was often cited. In one instance it was alleged that ASTM was located in Pennsylvania due to specific features of the State Constitution which granted liability protections to standards published with a "full consensus" and that was often taken back then to mean essentially full agreement in the community including to any critique from outside the Committee's official membership. However in 2010 only a small fraction of the Committee was taken as the "consensus".

Further flaws with the NASA testing surfaced later [3] and an appeal to ASTM's Committee on Technical Committee Operations (COTCO) revealed that in today's parlance a Committee may define a consensus in any way they wish, including calling five of thirty subcommittee members and 10 of nearly a hundred main Committee members a consensus.

In the 2010 dissent [3] alleged flaws in the NASA testing [2] were elaborated and then in 2014 [4] was revisited and extended to question G 124's fitness for use. These three arguments [1], [2], and [4] are included in this collection and the latest materials were further developed in the final analysis in this book [5] to conclude G 124 *is* unfit for use. The intuitive (yet writer-alleged wrong) obviousness and the popularity of NASA's reputation notwithstanding, this book has been compiled to facilitate understanding of incidents that may be aggravated by use of less than desirable metals.

All four of the writer's detailed arguments herein, admittedly overlap but also evolve. Each makes a progressively stronger case, with the fourth in this book, leading the writer to conclude and assert G 124-10 (and its re-approved G 124-18 version) are no longer viable.

Three of the four papers are almost as they were originally released modified only to remove or redact addresses no longer valid and to attain consistent format.

These analyses seek to stand on the shoulders of giants in the fire and combustion field (outside of ASTM G-4) rather than to break new ground. The writer can only hope he has done those forebears justice. However, this case against G 124-10 is strong even if flaws be found, or merely claimed, in any individual aspects of these papers.

References Revise

- [1] Werley, B. L., **“Drawing the Line on Fire Limits,”** Submitted for the Fall, 2002 meeting of ASTM Committee G-4 (10-12 September 2002), Marshall Space Flight Center, Huntsville AL 2002, 11 pages.
- [2] Sparks, K. M., Stoltzfus, J. M., Steinberg, T. A., and Lynn, D., **“Determination of Burn Criterion for Promoted Combustion Testing”**, *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres: Twelfth Volume, ASTM STP 1522*, Hervé Barthélémy, Theodore A. Steinberg, Christian Binder, and Sarah Smith, Eds., American Society for Testing and Materials, West Conshohocken, PA, 2009, pp. 80-95. [Also: *Journal of ASTM International*, Vol. 6, No. 10, Paper ID JAI102351]
- [3] Werley, B. L., **“Dissent and Protest to Revision of ASTM Standard G 124's Criteria for Defining Fire Limits: Influences of Ignition and Extinction Processes”**, Self-published paper, 2010, ~21 pages.
- [4] Werley, B.L., **“A Challenge to the Fitness-for-Use of Standard G 124-10 to Select Metals for Oxygen service’**, Self-Published Opinion, 2014, 15 pages
- [5] Werley, B. L., **“ASTM Standard G124-10, -18 is Unfit for Use”**, Self-published opinion, *The Saga of ASTM G 124; How a Standard Intended to Make Oxygen Systems Safe Became Unfit for Use*, Public service opinion, 2019, 48 pages.

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Drawing the Line on Fire Limits²

REFERENCE: Werley, B. L., “**Drawing the Line on Fire Limits,**”, Prepared for the Fall, 2002 meeting of ASTM Committee G-4 (10-12 September 2002), Marshall Space Flight Center, Huntsville AL, 2002, Public Domain 2020, 11 pages.

ABSTRACT: The measurement and use of fire limits for gas mixtures is a long-established practice that nonetheless is often questioned. Fire limits for metals are newer and may be even more difficult to measure and apply. Issues in measuring and comparing the two as they affect oxygen system safety are discussed.

KEY WORDS: oxygen, oxygen compatibility, flammability, fire limit, flammability limit, fire combustion.

The “modern” study of flammability is nearly two hundred years old. Davy [*I*]³ apparently first described a modern flammability limit theory in 1817 by asserting that it was when a gas mixture had a sufficient heat of combustion to raise itself to its ignition condition. Automobile internal combustion engines have operated pretty effectively within the “flammability limits” of gasoline for about one hundred years. And ASTM Committee G-4 has used fire limits in the safe design and operation of oxygen equipment for nearly thirty years. Yet today, as has been the case in other theatres for decades, there is debate as to just what a fire or flammability limit is?

If one turns to the scholarly literature, one may find it unsettling. Even now in 2002, one might even be tempted to wonder if there really is such a thing as a precise fire limit. And this wonder has been around for a long time both within the ASTM Committee and in the literature.

This quandary does not stop laboratories from measuring “limits” nor oxygen compatibility (OC) practitioners from using them. To paraphrase a famous U.S. Supreme Court Justice quotation, “We may not know what a fire limit is, but we know one when we see one.” Still there is little comfort in the use of fire limits, often leading to large safety factors being applied to their use.

Now there are many conditions which everyone agrees are clearly over the flammability limit. And there are also many conditions which everyone agrees are clearly short of the flammability limit. The problem is with the gray area that establishes the transition from

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² This paper was prepared for the Fall 2002 meetings of ASTM Committee G-4 on Compatibility and Sensitivity of Materials in Oxygen-Enriched Atmospheres on 10-12 September 2002 in Huntsville AL.

³ Italic numbers in brackets refer to the reference list at the end of the paper.

“over” to “short of”—namely where to draw the boundary line, if there is one to be drawn. The writer has recently voted negative on this same issue on a fire limit standard (ASTM G 124) ballot yet feels no great comfort that his position is correct or that the opposing view is either. If a degree of comfort were achievable, the engineering judgment of OC practitioners would be less challenged.

This paper attempts to review some of the available history and to offer insights into fire limits. This is more likely to add to the debate than it is to add to the resolution. Among the resources used will be old-standby references [1-6] and recollection of debates within ASTM G4 over its thirty-year history.

What is a Flammability Limit?

Ordinary dictionaries are silent [7]. They are also silent on the common synonyms: inflammability limit, explosion limit or deflagration limit. Numerous respected references discuss gas-phase flammability limits and even how they are measured but do not precisely define what they are.

Gas Mixture Fire Limits

Early flammability-limits were for real “flame” limits. Gases which produce visible flames were being burned. Early testing, as with much current testing, to establish flammability used glass tubes and experimentalists looked at the tube and judged whether its fill had burned. Some gases burned so timidly that the flame was hard to see, but it was there. But then as always seems to be the case, things got complicated. And the key questions still persist today.

Generally, the fire limit is the “precise” boundary where a fire can occur if started. But how much fire is necessary? Among the most respected and cited references are two legendary U. S. Bureau of Mines Publications: Coward and Jones [2] and Zabetakis [3]. Coward continued to write a condensed version for *Patty’s Industrial Hygiene and Toxicology* that was later taken over by Grumer [4] and probably continues to this day.

Coward and Jones (page 1) define the flammability limit by implication in a section titled **Conditions for Propagation of Flame in Mixtures of Gases** that warrants close examination here:

“When a source of heat of sufficient size is introduced into a weak mixture, some combustion occurs, even when the mixture is incapable of self-propagation of flame.”

Therefore, the limit is not established by the mere existence of “some combustion”, the combustion must be substantial. The second and third sentences of that same paragraph are:

“This is often visible as a ‘cap’ of flame which may be large if the source of heat is ample. The flame cap may be fixed in relative position to the source of ignition, as in a miner’s flame lamp burning in a gassy atmosphere, or may become detached from the source and float for a limited distance in a moving atmosphere, or may travel away 2 or 3 feet from an initiating spark or flame in a still atmosphere.”

The important conclusion is the final sentence of that paragraph:

“Such flames are not self-propagating, as they are extinguished when the source of the ignition is lost.”

So even though flame may travel for 3 feet, it is *not* within the flammability limit. This is the apparent basis for the Bureau of Mines adopting a four-foot-long glass tube for their test procedure. Several sentences later, after discussing how mixtures may not always “ignite” Coward and Jones note:

“As the test concerns the capability of the mixture to propagate flame not the capacity of the source of energy to initiate flame, it is axiomatic that the limits are unaffected by variations in the nature of and strength of the source of ignition. When statements are made that limits vary according to the means of ignition, it is clear that the observers used either such strong sources of ignition that the caps of flame gave the appearance of general inflammation or such weak sources that flame was not started in mixtures which were, in fact flammable. Under these conditions they were determining the limits of ignitibility, by the particular source of ignition they used, not the limits of flammability of the mixture itself.”

This is actually defining a second kind of limit. So as the nature of a mixture varies it may go through an ignitable condition and later as it becomes more reactive, it may achieve a flammable condition. Very few data are published about limits of ignition.

Zabetakis [3], in another legendary 1965 publication seeks to supplement the Coward and Jones work. His language becomes more precise than their’s while writing actual definitions:

“...limit-mixture compositions that depend on the ignition source strength may be defined as limits of ignitibility or more simply ignitibility limits; they are thus indicative of the igniting ability of an ignition source. Limit mixtures that are essentially independent of the ignition source strength and that give a measure of the ability of a flame to propagate away from the ignition source may be defined as limits of inflammability.”

In practice, these limits are used as thresholds one crosses over. But through the years there has been debate over this approach. When cavepersons first became familiar with combustion, they would have discovered there is a region where things do not burn and another region where they do, and it would have been logical and perhaps even genius to realize that there is a point where things cross-over. However, with a much more modern perspective, it is valid to wonder whether the transition is abrupt or gradual. Perhaps one or both kinds of limits are actually arbitrary points on a gradual curve of substantial width.

So think about it. For a period of history, candles were either lit or not. Then in lighting a candle one day, some finicky individual notices that the candle does not always stay lit. Sometimes it flickers for a bit and goes out on its own. And soon the issue of adequate ignition and candle condition both became valid parameters in successfully lighting the candle.

You need a candle that will burn (indefinitely) and an igniter that will give it an adequate start.

Some of the debate over flammability limits as “fundamental properties” are reviewed circa 1961 by Lewis and von Elbe (page 310) [5]. Indeed, there have been many layers of sophistication added to Davy’s original insight [1] by heavy duty scientists and engineers, yet today, most of the practiced combustion technology still rests most heavily on empirical measurements that still retain a degree of uncertainty.

Notice that in theory, there is no substantial difference between burning beyond the influence of the igniter and indefinite combustion. In a single paragraph, Glassman [6] page 142, notes that Coward and Jones tests with “high energy starting conditions are such that weak mixtures will be sure to ignite” (be taken above the ignition limit) and that for the glass tube, a “4-ft length is chosen in order to allow an observer to truly judge whether the flame will propagate indefinitely or not.”

The latest publication reviewed, that by Grumer [4] from the Bureau of Mines, still carries these same sentiments.

Other Fire Limits, Same Problems

Very early in its life (1970s), ASTM Committee G-4 adopted the use of oxygen index data for oxygen systems. They had been in use in industry for years (not decades) and had proven effective for ranking materials and, with much greater difficulty, in some cases for establishing actual use conditions.

The oxygen index is a fire limit that can be related to premixed-gas fire limits. When one dilutes the oxidant (oxygen or air) with a diluent (a material not reactive, typically nitrogen) that is used to measure lower flammability limits, one reaches a point where a flammable condition can no longer be produced with any amount of fuel, and it defines the minimum oxygen for combustion.⁴ This is a fire limit analogous to the oxygen index, in which the oxygen in an oxygen and nitrogen stream is reduced until one can no longer achieve a candle-like combustion of a vertical specimen. The test method is ASTM D 2863 *Measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion of Plastics (Oxygen Index)*.

D 2863 was used largely for quality control testing of plastics (after checkered use as a fire limit). Many years later (1995), ASTM G-4 incorporated the core of the D 2863 standard into its own version: G 125 *Measuring Liquid and Solid Material Fire Limits in Gaseous Oxidants*, and the writer prepared its first draft for ballot.

Here again, in developing D 2863, the same issues of defining the fire limits had to be confronted as for gas mixtures, and the confrontations were carried out at General Electric’s Research Division. After some confusion in the early revisions of the standard, the present criteria were published. Here, thanks to ASTM style mandates, an official “standard” definition was established:

oxygen index—the minimum concentration of oxygen expressed as a

⁴The writer is currently seeking to replace the current terminology for this and other fire limits with a more precise system called FLLAME (Fire Limits for Linearly Afflicted Minds, Everywhere).

volume percent, in a mixture of oxygen and nitrogen that will just support flaming combustion of a material initially at room temperature under the conditions of this test method.

So how does one establish “just support” of “flaming combustion”? First, the specimen must be “well lighted” that is to say must be over the analogous “ignitibility limit”, and this is taken to be in some cases if flame covers the entire specimen top and in other cases if the specimen burns a distance of at least 20-mm. Second, combustion must persist for a specified length or time above the fire limit (the oxygen index). For many materials the time criterion is 3 minutes and the burn length is 50-75 mm.

However, the definition is weak, because there is a qualifier missing that is clearly specified in other parts of the standard and in greater detail in earlier revisions—that of equilibrium combustion. The combustion while burning for the three minutes or 50-75 mm length is in equilibrium. When the test is terminated, if the tester so wishes, *the specimen is still burning pretty much as it had all along.*

In the mid-1990s, ASTM G-4 sought to expand and clarify the use of oxygen index tests by extending the procedure to additional specimen types and oxidant types and by elaborating on many of the details from the perspective of loss prevention use. In particular, the discussion of “equilibrium combustion” was detailed. The G-4 text in G 125 argued that “equilibrium combustion” was when:

“the combustion along this distance [50-75 mm] and through this time [3 min] must exhibit equilibria and create the impression that it would proceed on for an indefinite period were the sample longer or were more time to be allowed. The fire need not be calm and uniform to qualify as ‘equilibrium;’ however, any variations in intensity or erratic nature should not be systematically decaying.”

Therefore it is necessary to closely observe the combustion of any specimen that is not allowed to burn to completion if one wants to consider the test as a positive result. And it also requires the observation of combustion of specimens that *do* achieve the time or distance criteria and even go on to completely burn the specimen in case their combustion was decaying throughout and might actually be negative results. The writer believes this is the intent of standard D 2863 also, though it is not as clearly described therein.

ASTM G 124, Same Story, Different Day

The use of the oxygen index led many to experiment with still other flame limits in the ASTM D 2863 apparatus and in analogous pressurized systems. This led to reports of “Pressure Thresholds” [8]. These fire limits were treated like oxygen indices, except that the oxidant concentration was held constant and the pressure was varied to establish the threshold. Ultimately, in 1995, a procedure (G 124 on *Determining the Combustion Behavior of Metallic Materials in Oxygen-Enriched Atmospheres*) was developed based on the specific apparatus used by the NASA WSTF oxygen laboratory.

This procedure also held pressure (approximately) constant and conducted multiple tests. The original (and current) standard defines the threshold pressure as follows:

“The minimum gas pressure (at a specified oxygen concentration and ambient temperature) that supports self-sustained combustion of the entire standard sample.”

And it goes on to define self sustained as:

Combustion that consumes a sample to the point at which the sample holder affects further combustion (assuming sufficient oxygen).

The discussion in the standard allowed that in some cases where a specimen might quench due to the heat capacity of the holder, test results that were slightly less than complete could be scored as complete combustion.

These threshold-pressure tests, and most tests of metals in general, exhibited some major differences from standard oxygen index tests. One major difference was that the standard oxygen index test employs upward oxidant flow and top ignition, whereas, the threshold pressure tests employ downward flow and bottom ignition. The former configuration had been chosen because most polymers burn through evaporation and the combustion products at the top are carried upward and away. Indeed, in the few cases of polymers that melt when they burn (for example: nylons) the result and events during a test were erratic. So in adopting the threshold pressure test, which was intended principally for metals, and because most metals melt when they burn, bottom ignition was chosen so that melt would drip away (carrying heat of combustion with it) rather than drain along the specimen potentially pre-heating it.

Note that because of these specific choices, neither the polymer nor metal test configurations sought to establish the most flammable condition. By Davy’s earliest insight, the most flammable condition is achieved adiabatically, when the retained heat of combustion and its effect is maximized. That is accomplished by insulating the specimen, retaining the combustion products nearby, increasing surface-area-to-volume geometry, and the like. But it recognized that most real-world combustion does not occur adiabatically.

Early industrial testing [8] also employed a downward flow to also carry away any hot gas combustion products consistent with the rationale of the oxygen index test (but this latter assumption later proved to be false in that even with a significant average downward gas velocity in the apparatus, the convection currents driven by the hot buoyant combustion gases cause a local upward velocity to dominate). So therefore, the ASTM test which employs a nominally stagnant oxidant also allows the generation of a strong upward convection flow along the full length of the recommended specimen (150-mm long rods, 3.2 mm in diameter).

The body of metals testing has shown them to exhibit a character much different than gas or polymer combustion. For years there has been debate as to what the preferred specimen lengths should be and what the criterion for a positive combustion test should be. Indeed, for some metals, questions have arisen as to whether there might be a much larger gap between the ignition limit and combustion limit results than for gases and polymers. Finally, metal tests are much more demanding of time, effort and expense to accomplish, making it difficult to collect a wide spectrum of results with which to evaluate the procedure. Nonetheless, G 124 has enjoyed great success and is used widely in industry and government.

A Current Dilemma

A current draft revision of G 124 recently balloted proposes that the definition of self-sustained combustion (discussed above) be changed to:

“Combustion that consumes the test specimen, assuming sufficient oxygen, beyond the point at which the promoter influences the combustion of the metal. Combustion is generally considered self-sustained when the specimen burns more than 50-mm.”

The first sentence of this proposed new definition seems completely consistent with gas fire-limit work in which “combustion beyond the igniter influence” and “combustion that is indefinite” are essentially the same thing. However, are combustion “to the point where the test specimen holder is a quenching influence” and to “beyond the point of igniter influence” the same thing? And if so, is combustion that extinguishes at 50-mm or more a result that should be taken as “combustion beyond the igniter influence”?

“To the holder influence” versus “beyond igniter influence”

The existing definition of self-sustained combustion in G 124 appears renegade. It is neither the “indefinite combustion” nor “combustion beyond the igniter influence” that form the apparently equivalent parts of the limit definition for gas-phase combustion. But remember that metal combustion tests by G 124 are much different in behavior and the way they are conducted.

Namely: G 124 does not mention equilibrium combustion which is a crucial element of gas and polymer tests. This is not an oversight but may have been poor form. Since metals tests are by their nature difficult to observe (they are excessively bright, they obscure combustion with thick smokes, they are not smooth and often exhibit repeated dripping, etc), G 124 is predicated on a distance burned alone with no visual assessment of equilibrium combustion. In doing an oxygen index test, *any* specimen that stopped burning on its own would score as a negative, regardless of the period or length of its burn, unless it was observed not to be decaying in scale or velocity or intensity, that is, unless it could be argued that the extinguishment was abrupt and possibly due to an inhomogeneity in the specimen or other reproducible erratic mechanism.

In the case of a test by G 124, which can not be effectively observed closely, every result that does not consume the entire specimen by definition stops on its own. It is not indefinite combustion. Therefore every positive-score specimen was required to burn “completely”. Now the purpose of the apparently deviant clause allowing specimens to burn close to the sample holder and extinguish yet be counted as complete is because the heat balance can be very close for borderline combustion near the threshold and the sample holder might be a quenching influence, such that were the specimen longer it may have continued to burn. So near-complete combustion was scored as positive. Note that G 124 did not address at all (except by adopting rather long 150-mm specimens to facilitate likely self-extinguishment) those cases of decaying combustion that would score as a negative result despite burning to completion—a shortcoming therein (but at least an unavoidable and conservative error factor). So the writer would argue that for all of its apparent renegade appearance the existing

definition in G 124 is more in keeping with traditional practice than is a burn criterion lacking observation for equilibrium and known to score self-extinguishment tests as indefinite combustion.

However, there is another aspect that is troublesome regarding the use of incomplete combustions as positive results. The current proposal suggests using a 50-mm burn as proof the combustion propagated beyond the influence of the igniter. Other burn lengths have been suggested for this purpose. Is this suggestion reasonable? The writer would tend to disagree.

The thinking to this can only be surmised. Clearly some people feel that since the igniter heat is transferred to the tip of the specimen “briefly” and because the thermal profile would be pretty steep near the tip, little of that heat would conduct to a distance of 50-mm from the tip and so its influence should be nil at that 50-mm point. It is important to remember that experimentation with gas mixtures considers the influence zone of the igniter to extend *up to three feet* from the ignition source, a distance that might seem counterintuitive to those who find the influence of the much more intense metal igniter to extend less than 50 mm. One would not mind holding their hand three feet from an igniter flame, but this one recommends against holding a specimen 50 mm from the tip during ignition. This is a flawed analysis that also overlooks some of the major differences between metal combustion and gas-mixture combustion in other critically important ways.

In gas mixture combustion, and to almost the same extent with polymer combustion, the igniter is virtually exclusively a rapid heat transfer. This is not nearly the case with metal combustion.

Common metal ignition frequently employs the combustion of promoters of metals differing from the test subject chemistry. Differing metals are chosen so they will burn in the atmosphere in which the metal itself does not burn and for other reasons also. Oftentimes catalytic metals such as platinum, palladium, or high temperature producers such as aluminum are used. And still other important materials may be present in the chosen promoter even if their chemistry is close to the test specimen's.

Consider an ignition that forms a molten droplet comprising the igniter metals mixed with molten metal from the specimen. When the droplet falls away, a portion of the droplet is left behind that may mix uniformly (or not) in the next droplet. There is controversy as to what fraction is left behind and how much mixing occurs, but some remains that contains a portion of the igniter chemistry, plus some of its heat transfer, and indeed, some of the igniter material may still be reacting and transferring new heat. And it is not outrageous to suggest that mechanisms may be present in some cases that act to retain a disproportionately large amount of the original igniter material. However, assume each succeeding droplet carries away a similar fraction of the igniter materials. If a significant fraction of the whole droplet remains behind with each drop, then a large number of drops may have to occur before the chemical influence and any afterburning of the igniter is eliminated. For 3.2-mm rod, a 50-mm length does not represent the formation of a large number of drops during combustion to purge the igniter influence.

Furthermore, as discussed previously, when ignition occurs there is a powerful buoyant upward convection along the specimen. Materials from the igniter may deposit or condense on the surface of the rod as well as convect heat to it. When combustion proceeds upward these deposits will be fed back into the combustion process and may again alter any number of properties (favorably or not). Former associate Mike Lanyi [9] has often stressed the pow-

erful effect that sulfur can have on steel slag and even at rather low levels. It can greatly reduce the slag surface tension and therefore the mechanics of droplet release. This may operate to either inhibit or enhance combustion, situationally (and may even explain why self extinguishment sometimes occurs after surprisingly long burns).

Either of these effects could have influence (heat transfer, catalysis, physical property effects or continued heat input) easily at distances of 50-mm and more from the ignition site. For these reasons and others, the presumption of igniter influence dissipating within 50-mm is difficult to validate, even if one could rule out simple heat transfer to that point. Therefore the use of a positive burn score for 50-mm extinguishment that does not also confirm equilibrium combustion with direct observation is difficult to accept.

Following the observation of a stunning effect due to flowing oxygen through stainless steel tubing [10], the writer encouraged sleeved combustion tests with annular oxygen flow so that a higher gas velocity could be preserved near the surface of steel rods. At even low gas velocities, this would preclude convective heat transfer and chemical contamination of the rod's surface. And perhaps alternative "clean" igniter schemes less likely to introduce altered chemistry should be tested also in the pursuit of well-behaved combustion (if such a thing exists). But these can only be an effort to improve the results in the future and provide no assistance with the use of the test today.

A statistical argument

Regardless, of whether the influence of the igniter can be rationalized or not, there is a natural tendency among those who do metal combustion tests to predict the results. Often when one conducts a long series of tests which seem to burn only a small distance, an outlier occurs in which a long transient propagation or even a complete specimen combustion occurs. It leads one to surmise that if a short series of tests produces even one long transient propagation, then, sooner or later, if testing be continued for long enough, a complete combustion will obtain. So perhaps this is an alternative basis why significant transient combustion should be scored as complete combustion.

To the writer's knowledge, there is neither a strong case to defend or refute this surmise. He has observed the same thing and been tempted to the same conclusion. But he has also seen test series in which only a small fraction were long transient combustions, and he has repeated the same long series at progressively and significantly higher pressures, only to find the same infrequent long transient results at the higher pressures also.

An Important Nexus

Oxygen compatibility practitioners (OCPs) are apples living in a world of oranges, and it causes no end of grief. There is no doubt that the overwhelming preponderance of those who study flammability (yet very curiously not those in the U.S. Bureau of Mines who have been so central to the subject) are seeking to produce combustion. They want to burn the trees, the gasoline, the rocket fuel, and a myriad of other potential fuels and wastes. OCPs want to prevent combustion and save lives and such (as does the U.S. Bureau of Mines). And the two goals are not the same. This is the OCP's dilemma. To burn or not to burn.

So fire-limit data are most often collected and used to establish those situations in which a material (tree, gasoline. etc.) will completely burn and render its full heating value. OCPs

are trying to use these same data to establish a condition in which that same material will not burn (in the least, if possible). This is not a small problem.

Many an incident in oxygen hardware has not burned indefinitely. A pipeline ignites and ten feet of pipe is consumed. Is that a “flame cap” that would be scored as a negative result in a large scale pseudo-test? Would it have been prevented if the pipeline operated below its *in-situ* pressure threshold as measured by G 124? If someone standing five feet from the ignition point of that pipe were to be seriously burned, they would draw little comfort from the fact that it was “only” a “flame cap”.

In many industrial processes that share the same goal as OCPs have for oxygen systems, they do indeed use ordinary fire-limit data after applying a safety factor to achieve industrial safety, and they have been stunningly successful. In NFPA 69 [11], one is allowed entry into a region only if the air contains less than 25% of the lower fire limit concentration. It works! So the degree of success of ASTM G-4 should be no surprise.

However, the experience base for those other safety efforts is comparatively vast. Furthermore if one fears that the combustion of metals is categorically different, then can one still mimic the other practices with adequate results? If there is a much wider range between the ignitability limit and the fire limit, how does one choose safety factors? If the fire limit for metals is vague, so that one cannot draw a precise line as the limit, then just what is the best test procedure?

The traditional fire limit is the borderline condition at which a complete fire will just occur. The OCP would be much more comfortable knowing the borderline condition below which no significant fire will occur, that is the ignitability limit. This latter limit would require little in the way of safety factor for application, but it would be difficult to measure in a method that demands some significant damage in every test to assure the ignition threshold has been crossed. Indeed, today G 124 reports the lowest condition at which a complete combustion occurred and the next lower condition for which some number (currently at least five specimens) did not experience complete combustion. However, among those five “negatives” might be several which experienced fire caps that would be intolerable in an oxygen system if they were to occur on a proportional basis.

This is why the judgment of the OCP is still among the most crucial elements in designing a system. This judgment has a long way to go before it is adequately diagnosed and documented.

In the case of metals, but also for polymers and gas mixtures, OCPs, and indeed all of the other safety professionals would prefer limit data based upon the condition below which flame caps do not occur. Such limits may be intellectual concepts that do not occur in nature. But then maybe flame limits, themselves, are also in this same category.

Perhaps it would be a bold stroke to move to the measurement of ignitability limits. However, it appears the extreme cost of such an effort allows for no such tactic today.

Finally, keep in mind that OCPs use these fire limit data two different ways. One way is to set allowable use limits on specific applications, and the other is to rank metals for relative usage. The latter use has been validated for polymers and appears to be valid for at least some metals using the current definitions of fire limit. The use of a transient combustion limit may impact the rankings that the test may produce, and it is not clear whether these other potential rankings would be more or less valid than at present.

Summary

Among the most widely used of fire safety data are fire limits. The fundamental definitions of how limits are measured were reviewed. Established methods seek to determine where indefinite combustion to the point of completeness occurs. This principle was a factor in development of ASTM standard G 124. However, there is debate as to whether a complete combustion limit is most practical to measure and to apply, and so the merits and practicality of alternative limits were reviewed. Precise limits where fire does not occur may not exist or if they do exist, they may be too low for any practical application. Current interest is in simplifying the measurement of limits by G 124 using inferences of complete combustion conditions by extrapolation of partial combustion results. It is discouraged. Alternative efforts to seek better-behaved combustion is recommended for the more distant future.

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Dissent and Protest to Revision of ASTM Standard G 124's Criteria for Defining Fire Limits: Influences of Ignition and Extinction Processes:²

REFERENCE: Werley, B. L., “Dissent and Protest to Revision of ASTM Standard G 124's Criteria for Defining Fire Limits: Influences of Ignition and Extinction Processes”, self-published opinion, [REDACTED], 2010, public domain 2020, 32 pages.

ABSTRACT: In 2010, a revision of ASTM G 124 on promoted combustion testing of metals was adopted that changed the criteria for a positive self-sustained test from complete combustion of a 6-in. (152-mm) specimen to 1.18-in (30-mm) or more of combustion. Two bases for the change are challenged and equilibrium combustion is asserted as the more valid arbiter.

KEY WORDS: promoted combustion, self-sustained combustion, pass-through heat, oxygen compatibility, heat affected zone.

If one places a very combustible fuel material in an oxygen system and ignites it, it may, and often very probably will, burn and cause an incident with the possibility of explosion, potential injuries and secondary fire in the environment. Something to be avoided. The extent of the damage will be related to the amount of fuel material introduced and burned among other factors. But in some cases, an oxygen system itself may also be a fuel of variable combustibility if ignited. In this case, the hazard is related to whether the system will resist ignition or combustion, will lead to burning of a little (will experience transient “stimulated” combustion the way a nuclear reactor might be tickled to burn at a low level) or a lot (will experience self-sustained combustion the way a critical mass of nuclear fuel might yield an explosion). In the most extreme of cases, the combustion may sustain until major portions of a system are burned.

For more than twenty years, there have been two schools of thought within ASTM Committee G4 as to the best way to measure fire limits of solid and liquid materials. During this time the Committee's primary standards for measuring fire limits (*G124 on Determining the Combustion Behavior of Metallic Materials in Oxygen-Enriched Atmospheres* and *G 125 on Measuring Liquid and Solid Material Fire Limits in Gaseous Oxidants*, the latter based on the also-adopted *D 2863 on Measuring the Minimum Oxygen Concentration to Support Candle-like Combustion of Plastics [Oxygen Index]*) have employed complete combustion of

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² This paper was prepared for self-publication on the writers current web site: [REDACTED].

³ Italic numbers in brackets refer to the reference list at the end of the paper.

the test item (with some limited sophistry applied to the meaning of “complete”) to infer a positive-burn, self-sustaining propagation, test result (that is, one at or above the threshold, at or beyond the fire-limit). Anything less has been treated as a negative result, even if there was appreciable transient (“stimulated”) combustion, *unless it could be argued that there was a completeness aspect to the nonetheless incomplete combustion.*

However, there has been a strong counter opinion that when there is substantial combustion following a valid ignition that results in appreciable fire travel, that it signals a high likelihood that either a sufficiently long series of tests would ultimately yield a complete combustion (and even if not would serve as a more conservative indicator of a self-sustained combustion threshold) or that the test was on the very verge of a complete combustion anyhow. By allowing a substantial propagation to impute such an ultimate result, a more conservative limit is, indeed, established, and the test time and cost can be considerably improved. This second perspective is bolstered by a long standing analysis of combustion behavior that is quite plausible. However, if stimulated, or transient combustion is scored as self-sustained combustion, then desirable and even preferable materials may be excluded from use

For several years there has apparently been a renewed and reenergized debate within the attending membership at ASTM G4 meetings as to whether the criteria in standard G 124 should be changed to replace the past criterion for inferred self-sustained combustion from complete combustion to a specified minimum transient combustion criterion. In 2002 the writer voted negative on a ballot to change the criteria. As of this writing, 2009/10, a second and third ballot from the attending membership have been launched to again seek this change and the last has succeeded following a vote of attending members to rule the writer’s solitary negative vote nonpersuasive.

The ASTM consensus development process may allow for further opposition, but this ruling may suffice and G 124 may soon publish with the new criteria. In 2002, the writer detailed the bases for his opposition [*1*]³ in the context of historical fire limit testing. Since then there have been several additional papers supportive of the change published that cover new territory and data and the writer has had access to a few of them but not others, and so further comment will be reserved on some to a later date. This opposing paper is supported by the 2002 [*1*] paper and two recent ones [*2,3*] also employing new analysis and data and posting near-simultaneously. They are intended as rebuttal to the ballot, two of its cited references [*4,5*] and earlier supporting papers [*6,7*] to again make and document the opposing case with new analysis as both dissent and protest. One recently obtained reference [*8*] cited in the ballot may warrant later examination.

This commentator is currently a corresponding rather than an attending member and is therefore not privy to the discussions that have led to this effort. G4’s meeting have become rather insular, G4 having abandoned its newsletter many years ago, and its minutes of meetings of which are usually either nonexistent or cryptic. Indeed, the ballot overview itself and draft standard merely defend the revision as incorporating some state-of-the-art developments. Although negative ballots were cast, in the spirit of seeking accommodation the writer has suggested (without endorsing the idea) that rather than scrapping or changing the existing standard, that a second new standard based on the same apparatus be considered that allows for use of the second approach. If truly valid for all intended uses, it might supplant

³Italic numbers in brackets refer to the reference list at the end of the paper.

the previous version and even if not fully valid with regard to self-sustained combustion might still be of value to the design of systems where even transient propagation might be a concern, and it perhaps could be called something like a measurement of the onset of (transient/stimulated) propagation.

Although unfamiliar with much of the meeting dialog, yet familiar with the early basis for the changes support, the writer remains an advocate and practitioner of the current complete combustion approach, but recognizes that it, too, is flawed (and that upgrades to perhaps an “equilibrium combustion” criteria as outlined in the 2002 paper [1] and in less detail here may be warranted). However, when data of any kind are employed in an oxygen system evaluation, the ASTM G4 approach is to place the onus for the evaluation on the judgment of the system analyst. To that end, either kind of data can be prudently used, individually or together, however, the judgment and safety factors or margins that might be appropriate may differ depending upon the kinds of data that are available.

On the one hand, perhaps the writer’s concerns will someday become reconciled and the revision will be warmly embraced.

On the other hand, perhaps someday ASTM G4 may elect to deploy two forms of fire limit standard based upon the same apparatus and procedure as employed currently in G 124, however, which apply both sets of criteria for assigning the fire limit. It is not unusual for ASTM to publish variations on a similar theme like this and the G4 Committee itself already publishes its standard G 125 (which is also a fire limit standard more closely coupled to equilibrium combustion) and it employs the identical apparatus and procedure of D 2863 except that it supplements some techniques and elaborates upon the way the results can be interpreted to cope with shortcomings in the use of a complete combustion (and/or minimum duration of combustion) criterion. This dissent explores the analogous approach to upgrading G 124 through close observation or different inferred observations.

However, this effort also considers potential flaws in the way data are collected with G 124 and hardware or specimen controls that may be more important than the criterion.

In many cases, the limits measured with the G 124 system doing the test in any of the potential ways yield the same numerical result, but they may not be identical in *every* case, and if both are valid, the ways in which the two approaches would be applied could be different. If G-4 ever takes this approach, in time, the exceptions and techniques for applying both kinds of data will hopefully evolve and perhaps ways to validly convert between them will be developed and proved. This is also a beginning effort to that end.

ASTM Consensus

ASTM publishes “consensus” standards. A consensus is often taken to mean “general” or even unanimous agreement. Some ASTM standards publish without trace of opposition. However, while ASTM procedures require all opposition (whether from within or without the committee) to be considered, standards can publish with far less than unanimous agreement and are still called “consensus” because all parties agreed to accept the ASTM procedure even if they do not accept a particular standard, per se. In the extreme case, standards can in principle publish with nearly fifty percent of the voting committee in opposition. Nothing approaching this latter extreme has ever happened in the G4 collegium. Indeed, accommodation has been possible in most cases, and protest has been minimal in others.

ASTM Standards do not mandate a statement within standards as to the robustness of the consensus that produced them or whether there is dissent in the oxidant safety community, perhaps they should. Because of that lack, in this case, solitary separate dissent is being registered here.

Historical Fire Limit Measurement

Fire-limit testing has a long history (going back to at least 1817 [9]) and focuses almost entirely on homogeneous gas phase mixtures of fuels combined with air. Perhaps the largest amount of testing has been performed by the U.S. Bureau of Mines and their early works are famous [10,11] and are still the basis for much of the practicing fire-safety knowledge that exists today, and most of that knowledge and practice is empirical. These works are detailed to a much greater extent in the writer's 2002 paper [1] but will be briefly recapitulated here. Lesser amounts of testing by them and others employ the addition of diluents or use of pure oxygen, and a relatively tiny amount of work employs oxidants other than oxygen (F_2 , N_2O , NF_3 , O_3 , Cl_2). To the writer's knowledge, virtually all of these data are based upon a complete combustion criterion (with sophist aspects) that is intended to signal the threshold at which a fire might sustain combustion indefinitely.

In the 1960s, a significant body but nonetheless comparatively small amount of new testing became available when the oxygen index test (ASTM D 2863) was developed. In this case, solid plastic specimens were placed in a flowing stream of a gaseous oxidant (usually nitrogen mixed with air or oxygen) and top-ignited. This D 2863 standard mimicked the historical complete-combustion practice for gas-phase fire-limit measurement. In the style of gas-phase testing, with good precision, boundaries could be measured above which the specimens would burn completely or for which complete combustion (intended to be equilibrium combustion) could be inferred from the observation of combustion (intended also to be equilibrium combustion) or for a substantial period of time (three minutes). In other words, a candle did not have to be completely burned to score as self-sustained combustion.

The oxygen index test was originally intended to serve as a fire-safety quality control test. As a result, most of its testing was applied to relatively flammable plastics used to make common commercial goods, and most of which burned much like a candle, but for which there were important exceptions. However, when applied to materials that are of interest to oxygen systems, as well as to liquids, powders and pastes, several complexities and paradoxes were identified that led the G-4 Committee to the later publication of the derivative G 125 standard with its more sophisticated and elaborate interpretations relating to equilibria during the combustion.

Most gas phase fire-limit test procedures employ long propagation distances (most use 36-40 inches—about 1 meter tubes). They also use strong ignition, usually in the form of an open flame. It was not uncommon to observe a gas-phase mixture ignite and burn an appreciable distance along the (typically glass) tube but to extinguish before reaching the full length. One explanation for this effect is that the strong ignition employed can cause an overheating or other modification of the local gas mixture, in effect giving the combustion a desired "push", and thereby widening its fire limit locally. The extinction can result when the effects of the ignition dissipate (or more abruptly when other erratic effects or luck interfere).

However, as the combustion proceeds, four related consequences are possible. First, the “push” energy can be supplemented by energy from the specimen’s combustion and the combustion intensifies (but can later stabilize at a more intense level). Second, the push energy is “dissipated” (although the writer has recently proposed a more sophisticated view of the ignition energy as sometimes being “incorporated” into a “pass-through energy” [12] rather than being fully dissipated), Third, the fire comes to an equilibrium combustion condition in which there is just enough new energy (including pass-through energy⁴) to sustain the combustion. Finally, fourth, the “push” energy truly is dissipated even if temporarily supplemented by stimulated combustion, and the combustion extinguishes even if it has traveled an appreciable distance. And indeed in the latter gas-phase tests that propagate an appreciable distance, in many of these in which the combustion could be visually observed, the tester might notice that the fire is decaying in intensity or propagation rate or scale or that some other parameter is deteriorating, which would be an additional strong indicator that the combustion was not equilibrium and therefore the limit had not been achieved. These latter results are referred to in the literature as “flame caps”.

“Completeness” Sophistry

Even in gas phase tests, sophistry is often applied to the meaning of “complete combustion”, so as to allow scoring of some “incomplete burns” as self-sustaining. An important example of this is in the upward combustion of hydrogen [10].

When a hydrogen/air mixture is burned downward in air, it exhibits a fire limit of about 9%. However, when it is burned upward, a curious phenomena is reported. The gas phase mixture does not burn “completely” near the fire limit. The fire flame-front propagates “completely” from one end of the vessel to the other, but it does *not* burn completely throughout the full cross-section of the vessel. It “tunnels”. Instead at a minimum concentration of about 5%, the flame exhibits a cellular appearance (the writer has seen impressive photos but can not presently locate the reference). The fire proceeds as if small cells of local combustion are bubbling upward (as they apparently are in fact).

In the case of hydrogen, its extreme ability to diffuse (because of its much smaller mass and therefore much greater velocity than for other gases at corresponding temperature) allows it to concentrate itself in real time during combustion. Apparently, as fire is initiated in a gas mixture that is below the fire limit for downward combustion, the ignition energy locally widens the fire limit and allows a transient combustion to occur. This transient would normally be expected to dissipate and extinguish, however as hot burning gases bubble upward under the effect of buoyancy, the heat dissipates into the surrounding volume, and it increases the diffusion of hydrogen from the surrounding regions into the flaming cells where the extra hydrogen is reacted into larger slower molecules that do not diffuse back as quickly. And this selective migration of hydrogen towards the fire actually significantly elevates the hydrogen concentration in the flame zone and depletes it in the surrounding area, thereby establishing an equilibrium of sorts in the combustion.

In upward propagation, the actual (rather than superficial or calculated) hydrogen

⁴ Equilibrium combustion requires a certain amount of “preheat” to in effect “ignite” the incremental fire. Since an initial ignition energy is required, then at least some fraction of that initial energy must pass from increment to increment, and since this preheat energy can not be tagged for identification, one can view the transfer of energy at each step to be a portion of the original heat that is being “passed through”.

concentration that burns in the flame zone is doubtless higher than the average that is reported as the fire-limit.

In downward combustion, the effect of buoyancy is in the direction opposite to the direction of the flame-front travel. Therefore any enhanced diffusion of the hydrogen below the flame front is more uniform throughout the vessel cross section, and the propagation occurs throughout the entire vessel which then requires the higher concentration.

Hence in upward tests of hydrogen mixtures, propagation that passes completely from one end of the vessel to the other was scored as “complete” therefore self-sustaining combustion even though it did not pass through the complete specimen nor necessarily burn all of the fuel, but it did exhibit crucial equilibrium behavior. This interpretation was possible because the glass vessel used allowed for visual close observation of the combustion.

Analogous thinking is applied in ASTM G 125 which allows cups of burning liquids to be scored as complete combustion if they can be observed to burn in equilibrium combustion for significant periods or can be rationalized to have consumed a “complete” fraction of a distilling starting fluid. If the liquids contain a spectrum of constituents, the residue from one test can even sometimes be retested at more severe conditions and exhibit subsequent “complete” combustions of further residual fractions. The first test elevates the oxygen index of the second test.

Similarly, some solid materials that are tested can leave behind residues, often chars, for which a subsequent higher fire limit can be measured.

And perhaps one of the most impressive examples of “complete” yet incomplete combustion is in the burning of naps from fabrics. In elevated oxygen, the naps of fabrics have been seen to ignite and burn rapidly in a flash fire that often serves as an igniter for the rest of the fabric [13]. G 125 would allow a fire limit to be measured for the burning of the nap, scoring it as complete combustion, even though the vast majority of the specimen did not burn. This same distinction that applies to the flash fire in a fabric nap, is the thinking in tests for flash and fire points of liquids.

Solid and Liquid Tests

When conducting the Oxygen Index (OI) test on rigid specimens, one can also observe results analogous to flame caps. In the OI test of polymer rods, the most common specimen length is 3-in. (50-cm). While this seems much shorter than the 36-in burn length used in gas phase tests, the gas-to-solid conversion rate for many materials capable of vaporizing is on the order of up to at least 800 to one, so the number of linear molecule-to-molecule combustion steps in these polymer tests (if the polymer were vaporized) can be equivalent to as much as a 2400-inch gas phase specimen. In other words, if one were to freeze the fuel gas in a standard 36-in. gas test into a solid rod its length would collapse to only a small fraction of an inch or into a rod of negligible diameter. Nonetheless, the three-inch specimen length has proven adequate for many polymers while many would prefer a still longer 6-in length or even more for some materials and especially for metals.

Here again, the nature of the igniter and the ways in which it launches combustion can allow for at least three types of test results. If the specimen is above the fire limit threshold, ignition can yield an accelerating (sometimes explosively accelerating) test result that can also settle to achieve a terminal stable velocity. However, if the specimen is at the traditional fire limit, ignition can also settle to a steady uniform (equilibrium) combustion limit.

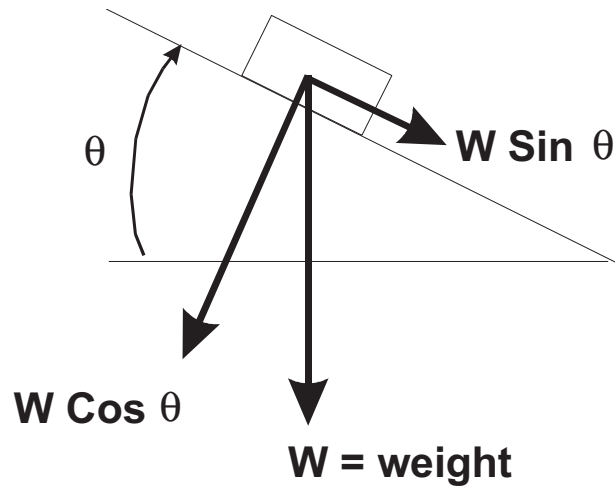


FIG. 1—Block on friction surface.

Finally, if the specimen is below the fire limit, ignition (if possible at all) can yield a decaying transient combustion that ends in extinction of the fire, sometimes very rapidly, sometimes not.

There are numerous variables that can affect these results. These variables include composition variations, igniter energy (size and composition) variations, and (random) unspecified effects and still others.

In some OI tests of specimens, one can observe obvious composition variations. Incompletely molded polymer sheet has sometimes been cut so that when different areas were tested they yielded different threshold fire limits (anisotropy). In the extreme, one could cut specimens and reliably predict whether they would extinguish or completely propagate at a single test condition. Therefore if one were to cut a specimen that comprised regions along its length of different local OI, the test results would be fickle. During a test one might observe (and has observed) the specimen combustion speed up and slow down repeatedly as it burned through the various regions. If one were testing a specimen that had been ignited in a low OI region, one might see it burn in local equilibrium and then suddenly (erratically) extinguish when it encountered a local region of higher OI. However, one might also see the same effect from a stochastic extinction. Conversely it might also accelerate suddenly. The latter might well indicate that a suitable threshold has been established. However, the former may require additional testing to establish a realistic threshold for use in the selection of safe materials.

The “Push” Energy Analogy

The “push” energy ignition model that has been cited here can be viewed as analogous to the model for static and dynamic coefficients of friction. To start a block on a friction surface sliding, Fig. 1, one must exert a greater force than is required to keep it moving. This lesson is most commonly learned when one’s car is stuck while driving on snow or ice

and one needs to accelerate slowly so that the greater starting friction can help pull the car out. Too much “gas” and the wheels spin without providing any significant traction.

If a block of weight, W , is placed on an inclined plane, Fig. 1, and the incline, θ , is increased gradually, eventually a point is reached where the component of force of gravity along the surface, $W\cos\theta$, exceeds the static friction and the block “breaks loose” and begins to move. This is one typical way of measuring the static friction coefficient. Indeed the block can accelerate because the force of gravity necessary to break the static friction is sustained and is then greater than the dynamic friction. Therefore, one can then reduce the incline under the sliding block, and if reduced far enough below the angle that initiated sliding, the block will reach an minimum equilibrium speed and at any still lower incline will stop. The static and dynamic coefficient can both be calculated from these two threshold angles.

If the block is on an incline that is less than the static threshold and it is given a sufficient initial push or impulse, then its static friction will be broken and it will slide down the incline accelerating for a while if the angle is greater than the dynamic angle (analogous to igniting a material that is above its fire limit), moving at a constant velocity if the angle is the same as the dynamic friction angle (analogous to igniting a material at its fire limit), and ultimately slowing and coming to a stop if the angle is less than the dynamic friction angle. This is analogous to igniting a material outside its fire limits. The greater the push, then the farther the block will move at inclines below the dynamic angle. However, at angles less than the minimum, the block will never move indefinitely, nor will it exhibit constant nor cyclic equilibria.

The motion of the block is thus analogous to combustion of a specimen. If the specimen is above its threshold then the energy of ignition, the “push” the igniter provides will launch combustion that will accelerate (but may later come to a constant level) and it will accelerate faster and to a greater intensity the farther above the threshold the specimen is. At the precise threshold, the ignition “push” will launch combustion but energy losses will slow the combustion to the equilibrium intensity. Below the fire limit, the push may still launch (stimulate) transient combustion, but its intensity will decay until the “push” energy is gone and then there will not be enough energy provided from combustion to offset the ultimate losses and it will ultimately extinguish.

A sliding block may also stop sliding for random or systemic reasons. It may encounter an obstacle. Similarly a specimen burning in apparent equilibrium may suddenly encounter an obstacle and abruptly extinguish. In this case, anisotropy of the inclined plane might appear as curvature that finds the sliding block suddenly at less (or more) of an incline. Indeed, equilibrium sliding can sometimes analogize to a sinusoidal surface in which the block accelerates down into valleys then decelerates up hills repeatedly and indefinitely, and similar equilibrium but variable combustion is possible (namely in the way typical specimens develop droplets that cause cyclic combustion). Several scenarios are shown in Fig. 2.

When specimen combustion tests can be visually or instrumentally observed, one can sometimes infer characteristics analogous to these to determine whether the combustion is equilibrium and whether any extinction is abrupt and random or the result of a progressive decay, or simply a run-down, of its push energy.

End Thermo Effects

The transient role that ignition produces can be viewed as an “end-effect” (an upset con-

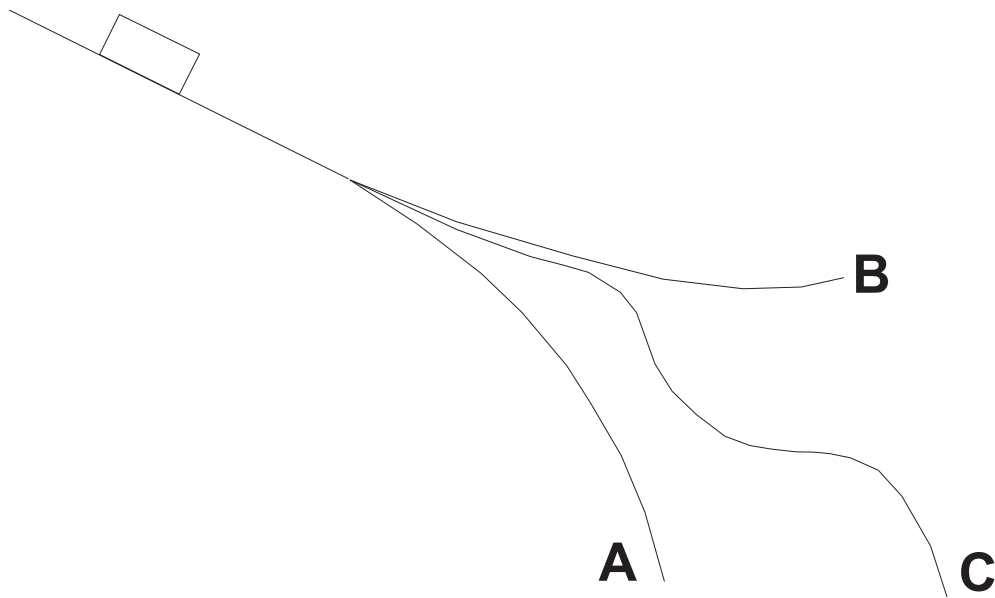


FIG. 2—*Sliding-block scenarios.*

dition that acts only “locally”, at the specimen end). Strong ignition has a “reach” that extends part way along the specimen. A second end effect is present at the opposite end of the specimen where the mounting can also upset any approaching combustion and has a “reach” of its own that extends some distance back along the specimen. Both end effects are important and, from among all the effects that might be possible in this very complex subject, are topics for simplification here.

Among the factors that can alter combustions near the ends of the specimen are the thermodynamics, the chemistry (including kinetics), and a range of physical phenomena (gravity, diffusion). The thermodynamic upsets will be focused on here.

When ignition is effected at one end of a specimen, it causes upset conditions in all three ways and more. With metal specimens, in particular, owing to their high thermal conductivity, the unburned material ahead of a fire front conducts heat out of the ignition and preheats the metal widening its local fire limits (and appearing as a elevated pseudo-heat of combustion [12]). An effective igniter needs to establish a specific preheat profile if it is to be optimally effective. If an ignition energy is large but too intense it may fail to launch equilibrium combustion as much as if it is too small. Thermal profiles along burning specimens have not been studied to any great extent and are not easy to study. Some modeling attempts have predicted gross expected features.

The second important feature is the end effect due to the method used to mount a metallic specimen. The mounting can also act in at least three ways on the minimum thermodynamics depending on whether it tends to conduct more, less, or the same amount of heat as would a much longer specimen. As a fire front burns toward a specimen’s end, the thermal preheat profile that has formed will begin to heat the termination.

If the termination conducts less heat than a longer specimen itself would, the tip will in effect be insulated, its thermal energy will “pile up” and its temperature will rise (elevating the “pseudo-heat of combustion” locally), thus widening the fire limits near the termination and can cause an end-stage acceleration of the fire. This end stage acceleration can ensure complete

combustion of a specimen even though the specimen may be below its fire limit. This is a particular concern if the ignition of a specimen can preheat the full length of the specimen. And with some metals fairly long preheating profiles may be possible.

If the termination conducts the same amount of heat as a longer specimen would, then the fire will approach the termination more nearly as equilibrium combustion (ignoring other potential effects). And, finally, if the termination extracts more heat than would a longer specimen, then the termination will narrow the local fire limits (acting as a decrease in pseudo-heat of combustion) and may cause the fire to extinguish some distance before it consumes the complete specimen. It may alternatively cause a slowing of the fire (a shift to non equilibrium combustion) as it approaches the termination.

Other end effects can also alter the scenario for kinetic, chemical or physical reasons. For this reason, it is sometimes convenient to think of the specimen as having three parts: a launch part, a gage part, and a termination part. The “true” specimen can be viewed as the gage portion which is attached between the launch part and termination part, the termination portion of which is intended to mimic the heat transfer properties of the gage section. Hence if the gage portion of the specimen has burned “completely” the test could be scored as a positive. However, different specimens can require differing terminations owing to the “reach” of the preheating. Specimens of high thermo-conductivity would exhibit a long conductive preheat and so the effect of a mounting mismatch may be long. In comparison some specimens (like 300 series stainless steel) have much less thermal conductivity and so the “reach” of the mounting would be much less. All of these factors can be considered in scoring specimen test results. *Provided this behavior can be closely observed.*

In cases where long specimens are burned, the rising hot gases from the combustion zone may convectively heat a specimen and also produce later acceleration of the combustion.

In cases where a specimen can be observed visually or instrumentally, these three effects can be much more easily identified and weighed in scoring the test result as a complete or incomplete combustion, and therefore whether it is equilibrium or not. When adequate observation is not possible as is the case with many pressurized test apparatuses and for the combustion of some types of metals that obscure vision, scoring near-complete or extinguished combustions can be far more difficult.

A study of the equilibrium preheating zone for assorted specimens would be of value in making these assessments but is not available at present. These data are more important with regard to metals than for polymers owing to the much lower thermo-conductivity of polymers that lessens the end effects (although many polymers also extinguish short of their holders, especially when they are tested near the threshold).

Historical ASTM G 124 Criteria

When G 124 was initially adopted about two decades ago, it deployed a long specimen for its time (152-mm [6-in.]) and mandated “combustion that consumes a sample to the point at which the sample holder affects further combustion” in order to establish self-sustaining combustion and to score as a positive test. The combustion could not be closely observed in the high pressure vessel, and so the long specimen was adopted to ensure a rundown of the ignition effects to an equilibrium state, because of known thermodynamic upset effects as well as other chemical and kinetic and physical upset effects. Combustion was not required to actually reach the exact end of the specimen because of heat sinking associated with the mounting, in which

case tests well into the combustible region might actually scarf into the holder but then as the threshold was approached might exhibit extinction just short of the holder. However, at the time, these conclusions were drawn in the judgment of the workers in the field on the basis of large numbers of tests conducted, and not as the result of detailed studies.

Complete Combustion Versus Significant Minimum Combustion

The writer has participated for several decades in the debate over the definition of meaningful combustion lengths for positive tests in the ASTM G 124 standard. The recent ballot references supporting papers as the state of the art in metals testing [4,5,8] and some others will be reviewed in detail here.

A very early, perhaps the first, ballot of G 124 contained a short criterion for scoring as a positive test of something like 1.3 inches based on the work of Zawierucha et al. [6] and Steinberg [14]. One argument was that a statistical view obtained: if propagation went any appreciable distance, then a distribution function applied and for some number of tests however numerous, sooner or later, there would be complete combustion when a combustion event on the tail of the distribution resulted. This was again (2010) a part of the dialog over whether to change G 124 from a complete combustion criterion to a significant minimum burn-length criterion for positive tests.

Another argument is that the effects of ignition dissipate rapidly [4,5] and therefore any further propagation thereafter indicates an elevated risk in an oxygen system. Argument and clarification text proposed in the final ballot asserted that any combustion “beyond 19 mm was clearly burning independently of the ignition-promoter effect”. The second aspect therefore argues complete combustion is “overly severe” to define the threshold, and that by choosing a shorter criterion, a more conservative result is obtained.

Again, the writer is not familiar with the full details of the ongoing dialog within G4 on this topic but acknowledges that both of these arguments *seem* both reasonable and intuitive to the experimentalist who has conducted a long series of tests in which most yield fairly short propagation distances but then for which every now and then a fairly long propagation may occur. The writer has had this experience and has experienced the same inclination.

However, there are good reasons why historical fire limit practice has adopted self-sustained *equilibrium* combustion and therefore “complete” combustion as its criterion for defining fire-limit thresholds of gas mixtures. ASTM G4, however, has long maintained (with this commentator in strong disagreement here also) that gas phase combustion issues are of little relevance to the oxygen compatibility subject).⁵

To some extent, this perspective may derive from a dichotomy that has always plagued G4. Many data generated on flammability come from disciplines that are seeking to achieve combustion (for heat, for engines, etc) and therefore focus on assured combustion (self-sustained) while G4 focuses on avoiding combustion for safety and therefore might seem only interested in the thresholds for even incremental combustion. However, this commentator wishes to argue here (as he has in the past for the importance of gas-phase fire-limit analysis) that is *not* the case; both categories can be critical.

⁵In 2000-2003, the writer beseeched ASTM Committee G4 (and to lesser extent the even more insular ASTM Committee E27) to pursue a standard on gas phase fire limit interpretation and application, including the development of a PC utility to deploy and simplify ternary-diagram analysis. Support was scant and although a Task Force to consider this was launched, it was never heard from to date.

The writer would argue (as reduction to absurdity) that G 124 rightfully uses a strong ignition. That strong ignition necessarily causes damage to a specimen and stimulates transient propagation (with exceptions). But that it is bad practice to score a test as “flammable” when in some cases the amount of “propagation” observed is similar to and possibly in some cases less than the amount of damage the igniter alone causes.

In the 1960s there was a movement to improve automotive ignition systems, both by increasing their ignition energy to ensure more reliable and less polluting combustion and their power delivery rates to achieve greater efficiency (one paper found that minimum ignition energy halved when power delivery doubled). Tests programs were run with progressively more powerful electronics, leading one worker to protest that clearly if a lightning bolt hits an engine block, the block will ignite and burn and that they were approaching the point where if they were to increase the ignition system energy by just one or two more orders of magnitude, it would be unnecessary to put gasoline in the cars to drive them (an approach that might seem appealing today) since the spark energy would exceed the fuel combustion energy.

In oxygen safety as well, one key focus is upon propagation, ignition aside, and that is appropriate. Hence, both arguments beginning with the recent paper by Sparks et al [4] will be examined closely.

The “Reach” of the Ignition

As already noted, in the past G 124 called for “combustion that consumes a sample to the point at which the sample holder affects further combustion”. The holder can affect combustion in various ways such as in quenching flame, but in large part this wording is because its heat sink effect may disrupt the delicate equilibrium thermodynamics that are required at the threshold. As a result, a key property for any test is the distance to which a thermal profile extends beyond the combustion zone. If the heat balance is precarious, disruption and extinction may (but also may not) occur as soon as the profile begins to lose heat to the holder.

Sparks et al. [4], have attempted to define and measure the maximum amount of preheating the standard G 124 ignition device can produce in any common specimen. This was then used to surmise a minimum propagation distance beyond which the ignition heat is no longer influential, and therefore to recommend a “length of test sample that must be consumed to be considered a flammable material”. The length they propose is 30 mm (1.18 inches), and this is the new criterion that was successfully balloted for G 124 in 2010 based upon the Sparks et al. testing.

Sparks’s approach was to choose an ignition “event duration” that would apply to specimens that burn by dripping. The standard ignition was effected on select specimens, most commonly copper that were not flammable at their conditions and the igniter was allowed to produce a “significant drop of molten metal, promoter detachment, or consumption of promoter”. At that instant, the thermal profile in the remaining specimen was measured, and the profile extended farther up the specimen for copper than for other metals tested.

Sparks then reasoned (perhaps optimistically) that preheating of less than 260°C (500°F) was irrelevant to propagation (because it had not seemed to alter the fire limits in a series of stainless steel tests [15]). Hence the “reach” of the preheat was taken as the point at 260°C (500°F), at the end of the event duration point. He reports this was no more than about 19-mm (based on the maximum average measurement plus three normal sigma), and added about a

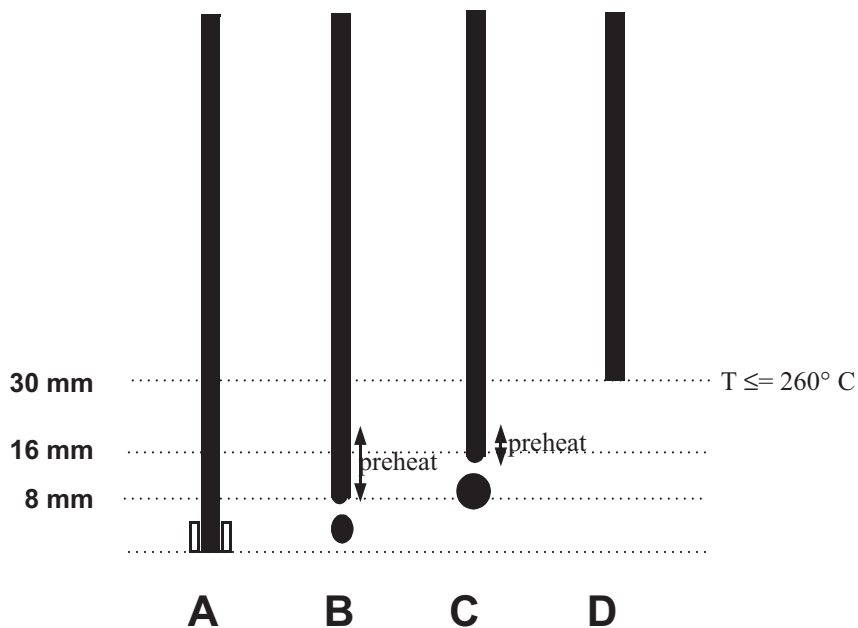


FIG. 3—Early specimen combustion behavior.

50% safety factor to arrive at the 30-mm recommendation, asserting that use of this limit “ensures all metals that burn a distance greater than 30 mm (1.18 in.) are burning independently of any promoter effects that preheated the test sample during the ignition process”.

Rebuttal 1

The measurements of Sparks et al. [4] are of interest and represent real progress but aspects of the reasoning and main conclusion must be challenged. Fig. 3 exhibits a hypothetical specimen under test. At point “A”, the pretest specimen with igniter is about to be ignited. At points “B” and “C”, are two scenarios in which the igniter has formed droplets about to fall. In “B” about 8-mm of specimen is melted/combusted (and this ignores additional volumes that the igniter material/oxide might add to the droplet size). In “C” about 16-mm of specimen is melted/combusted on similar terms. This hypothetical treatment will assume that in at least some cases (not including copper and Monel® 400), at least 8-16 mm of rod would be consumed at the threshold based on photos of burning metals and other data (in Sparks et al. [4] 316 SS data, it appears the igniter may have “consumed” the first thermocouple at the 7.6-mm point at a test pressure well below the threshold). However, in forming the droplets, the amount of specimen regression might vary greatly from droplet to droplet and material to material.

Sparks et al. assert that for an ignition duration that results with the droplet in the range of scenarios “B” and “C, that the point, “D”, indicated 30-mm above the original specimen bottom as shown by a horizontal line, is at no more than 260°C (500°F) with a 50% safety margin and probably even at a point no more than 19 mm above the original bottom of the specimen. The 30-mm point is taken as the maximum preheat. Indeed, that any combustion that propagates to the 30-mm point is therefore “burning independently of any promoter effects that pre-

heated the specimen” and therefore is “self-sustaining” *even if it extinguishes at that point*.

As a first rebut, this reasoning is apparently predicated upon the following syllogism:

- Heat from the specimen combustion produces a preheating of the metal ahead of a self-sustained combustion zone.
- If the preheating is diminished by the termination, then self-sustained combustion may cease early, before completion.
- Heat from the igniter produces a preheating beyond the igniter combustion zone.
- Therefore, if combustion does not cease at the end of the preheat zone [taken as the point at 260°C (500°F)], then it must be self-sustained.

A number of problems can be cited with this testing. For one, the early termination of self-sustained combustion may, but also may *not*, cause self-sustained combustion to cease *promptly*, depending on the run-down, the “push” or impulse. For two, the combustion and therefore preheating produced by the igniter is by design and definition “strong” therefore intended to be greater than for self-sustaining combustion. For three, the preheat zone and much less likely the ignition rundown distance (as described earlier) is not so easily estimated.

End Stage Early Extinction

To elaborate, the potential (meaning not at all certain) ability of the holder of a specimen to disrupt the equilibrium heat balance in, and cause extinction of, a potentially delicately balanced approaching combustion front is a far cry from extinction during strong ignition. The proposed “reach” of a strong igniter would indeed perhaps be a valid and conservative, but perhaps way too-conservative, dimension to use as a criterion for the much-less-robust equilibrium threshold combustion that extinguishes just as it approaches the holder. Indeed, the writer might be reluctantly wary scoring any combustion that stopped 30-mm short (Sparks et al’s. [4] preheat estimate) of the holder as self-sustained combustion.

Igniter Preheat and Other Effects

During ignition, a droplet is being forced into intense combustion (strong ignition) while the rod is being preheated. That first droplet and each succeeding droplet can be viewed as having a life cycle: that includes the stages: ignition, growth and detachment.

The first droplet's melting/combustion is forced (the combustion is given a robust “push” in earlier parlance) with excessive heat, which lowers its local threshold of combustion and allows it to burn more intensely than otherwise until it falls away. This is accomplished by using a promoter material like aluminum or magnesium or Pyrofuze, or thermite, that typically (but not always) has a higher heat of combustion than the specimen, has a higher adiabatic combustion temperature, and is present in a large amount. The first droplet that forms may be predominantly promoter material or some mixture of promoter and specimen. But it leaves behind a legacy in the form of that robust preheating (largely but not exclusively through conduction) in the rod above (and in actual practice it leaves behind other legacies, as well, in the form of remnants from itself and the initial droplet residue including possibly incompletely combusted promoter materials in potentially significant amounts).

Therefore an effective igniter will yield a more intense transient fire and presumably

more heat transfer than would result from that portion of the specimen that might burn to form later, or even the next, droplets.

As a result, when the first droplet falls, the igniter influence is *not* ended save for the legacy of the extent of limited preheating. The tip of the specimen must now be at or above the ignition condition for the specimen (and perhaps at or above other thresholds also), and it is doubtless well above. The preheat may extend only 19-mm above the original bottom but the degree of preheat of the specimen and any residue of the original droplet may be to a greater degree than that to which equilibrium combustion would produce for subsequent droplets. If the bulk specimen is not too far from its threshold for combustion, this second droplet forms and burns with less theatrics than for the first droplet. If far above the threshold, then each sequential droplet can be progressively more intense as the combustion “accelerates”. If near the threshold the superheated early droplets may decay in temperature. Indeed, Kurtz [16] exhibits photos of apparent decelerating combustion (Combustion for which starting “friction” has been broken significantly and for which the “decline” is significant and affecting a series of droplets). However, when pursuing and approaching a combustion threshold, the initial ignition droplet should be the most intense as the “push” [ignition] overcomes the starting “friction” [min. ignition temperature and min. ignition energy] and the combustion losses cause the “sliding” [the combustion] to settle down.

As a minimum, the first droplet will not usually partition the entire ignition energy but will pass some of the ignition legacy through to that portion of the specimen (perhaps roughly the 30-mm segment that Sparks defines) that will form the next droplet as a “preheat”. And this preheat may ignite the second droplet in the first step of its own life cycle in a fashion analogous to the first ignition heat. If the specimen is at or not too-far above its threshold or if the preheating has lowered the local threshold sufficiently, then the second droplet will burn and will act as though its heat of combustion were elevated (a consequence of the pass-through heat). As this second droplet burns, it can be viewed as a step in a kindling chain, as a second less-aggressive igniter (since its combustion should be more robust than for equilibrium combustion), and it transfers heat and has its own “reach” to form the third droplet, but again in the case of testing near the threshold, it may transfer less than was transferred to it. But a portion of this transfer may again be viewed as a pass-through (a legacy) of the original ignition heat. In much the way that feed-back operates, this operates as feed-forward. Below the threshold, the feed forward should decay, and above the threshold, the feed forward should build. This is like a continuous-dilution problem.

Each succeeding droplet that forms will receive preheat from the droplet before and a portion of that preheat may be viewed as legacy [pass-through heat] from the first droplet that is being continuously diluted and partitioned. If the specimen is at or above its threshold, then barring stochastic effects, bad luck, kinetics, physical effects and an approaching heat sink in the form a holder, each droplet should exhibit progressively less theatrics and the combustion should settle to an equilibrium condition in which it generates just enough feed-forward heat to burn and to pass through to the segment ahead to serve to preheat the next segment to the same minimum extent that the droplet itself was preheated to.

Sparks et al’s [4], analysis appears to assume that this combustion equilibrium is achieved in the very first droplet when that first droplet (at least for the igniters specified) is known to be much more flammable than would be later droplets of the test specimen alone. The writer is not aware of any analysis or observations that support such an assumption. Indeed, the whole accepted concept of thresholds being a function of temperature seems to imply that a lo-

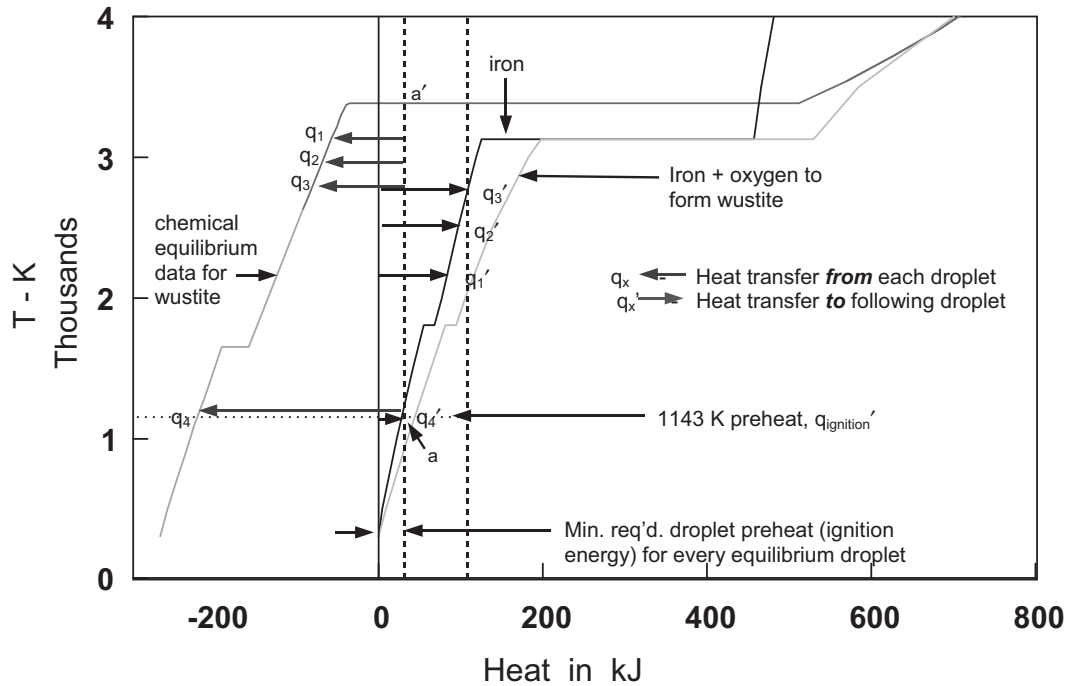


FIG. 4—Threshold minimum equilibrium heat transfer, from each droplet to its successor for 947Fe and 0.5 O₂ to form Fe_{0.947}O.

cal preheating of a specimen should spur local combustion, the same way that bulk heating of a specimen spurs general propagation in proportion to the scale of the preheat until that local preheating is dissipated. This interpretation is conservative and may ultimately be proven wrong in some cases but such proof should be sought.

A thermochemical model of this theoretical “push” process can be presented using software codes from NASA and Outukumpu⁵. This is abstracted from a more thorough treatment that is elaborated upon in a near-simultaneous manuscript posted by this writer [3].

For illustrative purposes only, one can treat the overall specimen combustion as a sequence of cyclic sub-combustions of approximately equal segments of the test specimen, and can consider the combustion of iron in stoichiometric oxygen to form wustite (Fe_{0.947}O). Fig. 4 based on the data in the simultaneous paper (Fig. 8 in [3]), exhibits the thermodynamics of combustion and factors in theoretical chemical equilibrium. The line marked “iron” represents the assumed heating of a quantity of iron for ignition (it is also the numerical value of the enthalpy of the iron with stoichiometric oxygen system for which the oxygen is kept at the standard state, room temperature condition). The curve marked “iron + oxygen to form wustite” represents the heating of both the iron and oxygen stoichiometric for wustite *without mixing them*. The curve marked “chemical equilibrium data for wustite” is chemical equilibrium data from both the NASA and Outukumpu software and thermodynamics from the JANAF tables for Fe_{0.947}O that is being heated toward the point of decomposition and partial leading to full vaporization. Above about 2700K, the curve is the calculated chemical equilibrium for a wustite product at vaporization temperatures and beyond.

⁵NASA software CEA (Chemical Equilibrium for Applications) and Outukumpu HSC for Windows 3.0.

In the style of the related manuscript, iron is taken as igniting at 1143 K (note: a temperature below its melting point that is defended in the literature). If a segment of the rod corresponding to that which forms a droplet is just heated (perhaps “on average”) to this point, requiring an amount of heat indicated by the arrow labeled q_4' , and if it were to burn adiabatically or nearly so, from an initial condition at point “a”, its adiabatic combustion condition would be at point “a'”. Since iron burns principally as a liquid (the oxygen gas combines with the iron and so the product is formed largely within the liquid and its approximate full heat of combustion is transferred into the liquid at “a”). At this point, in these conditions, heat losses to other than the droplet and the iron specimen are not assumed to be principal. The droplet would approach its adiabatic combustion temperature (~ 3300 K at atmospheric pressure and temperatures to a significant portion of this level have been measured). This droplet can then transfer heat to the succeeding iron segment, preheating it from room temperature (*and this analysis does not include any excess heat of combustion of the igniter itself beyond that which produced the initial 1143 K*).

As heat transfers from the subject droplet and it cools, the maximum heat transfer possible from it (whether the droplet achieves the adiabatic combustion point, “a'” or not) is indicated by the arrows, labeled q_1 - q_4 , drawn at several temperatures between the vertical line through “a” and “a'” and the darker upper cooling curve. If this droplet falls and partitions the heat of combustion (by removing heat capacity), the approximate maximum heat transfer possible from it at or above the presumed ignition temperature of 1143 K, is shown as the arrow “ q_4 ” (albeit at a point at which the droplet would not still be liquid, hence the actual physical maximum is somewhat smaller). If a portion (about 12%) of this maximum available heat (for this simplified model) is transferred into the next room temperature rod segment/droplet, and warms it to point “a”, then the cycle can just repeat itself with the next droplet. This is thermal equilibrium combustion (however, equilibrium combustion—not to be confused with chemical equilibrium—may be limited by other, higher, thresholds as well). If less heat than this transfers, the combustion can not sustain (but may not stop instantly due to thermal “inertia”), because the critical ignition temperature will not be achieved, and if more heat is transferred, then the combustion may accelerate (if there is no other interference) to a greater intensity.

Notice that the three arrows labeled q_1 - q_3 indicate lesser-than-maximum transfers possible *from* the burning droplet at higher temperatures, and indeed, the corresponding arrows q_1' - q_3' , are shown as heat transfer *to* the room-temperature rod segment that will form the subsequent droplet. Furthermore the arrow q_3 is the same approximate length as arrow q_3' and estimates the maximum temperature that could be produced in the next droplet.

A second dotted vertical line is drawn through the head of the arrow q_3' . Notice that if a segment/droplet is preheated to this level, either by the previous droplet or by the ignition energy, its combustion to point a'' would yield more intense and energetic combustion, and greater heat that can transfer to the next droplet than for the preheat or ignition to point a'.

When strong ignition is used, the rod segment that forms the second droplet, may be warmed (and in most cases is likely to be warmed) well above the ignition temperature. If it is not, then further combustion is not expected whether the rod is above its threshold (fire limit) condition or not.

Hence the rod segment that forms the second droplet, may be preheated only 30 mm, from the original rod bottom, but that very preheat may and for most strong igniters *will* produce a second droplet that will be more flammable than would be a droplet formed during equi-

librium combustion. Hence, as asserted before, the second droplet may act as an *in-situ* less-strong igniter. It may require several or even many droplets to fall before this excess preheating is dissipated (largely meaning partitioned) and equilibrium combustion is established or combustion fails. This is the threshold that needs to be determined to assess the full “reach” of the igniter, and as a decaying process would be a very difficult measurement.

Yes, at any time an erratic extinguishment may occur in conditions above the fire limit (if luck can produce extraordinarily long propagations, it can provide unusually short ones too), and in those cases equilibrium combustion may be present and the test should be scored as a positive. But until the heat balance point is obtained, any combustion may merely be transient.

Clearly a more sophisticated analysis than this is appropriate. However, with strong ignition, the amount of rod involved in forming each droplet may vary, higher preheats may yield surface tension variance that affect when droplets fall and how they partition the combustion and much more.

Nonetheless, this argues how for at least some metals, the legacy of the initial ignition heat may still be felt many droplets (well, at least several droplets as perhaps Kurtz’s [16] Figs. 4 and 5 may possibly document) after the first has fallen. Indeed, an asymptotic continuous dilution⁶ vestige of the original ignition heat may pass through *every* droplet.

Therefore, for the strong ignition used in G 124, it is very possible that the second (and perhaps still later) droplet will burn much more intensely and act much like a strong, if not robust, second igniter with a longer second “reach” itself, than would be the case for later droplets at the ultimate equilibrium combustion condition. QED.

A Tale of the Tail of the Distribution

Metal combustion tests similar to those of G 124 that are repeated do not always produce precisely similar results. Often there is scatter in the results that is, indeed, suggestive of a statistical distribution. If the testing is far below the fire limit, the scatter is in a clearly narrow distribution and the writer has observed a clear “central tendency” like this in his own past testing, but as the pressure or oxygen concentration is increased, the scatter increases and occasionally one can see a long propagation occur, or even more bizarre results. In the 1990s, the writer conducted one such long run of tests numbering to maybe two dozen or more at a single condition. Most were in a narrow band of propagation length (a central tendency) but a small number were to surprisingly long comparative lengths, nonetheless they were far short of consuming the complete specimen.

Such long, but incomplete results can be hard to accept as being below the fire limit. Can they merely be “flame caps” that indeed result only because of luck or some upset such as the strong ignition heat provided (perhaps passed through a large number of droplets) as the combustion ran down to an extinction? Or in the style of statistical analysis, can one calculate a mean and valid standard deviation and in turn predict that for a sufficiently long series of tests, that a result will indeed sooner or later propagate the entire distance and demarcate the condition as within the fire limit? So why not just score long runs (or as in the prior disputed analysis of Sparks et al. [4] even just runs that seem to trespass a “heat affected zone”) as predictors of self-sustained combustion?

⁶ The writer recalls a continuous dilution analysis that argued that *every* glass of water one drinks must contain hundred of water molecules that once passed through the kidneys of Cleopatra, but even now may or may not yet have reached equilibrium..

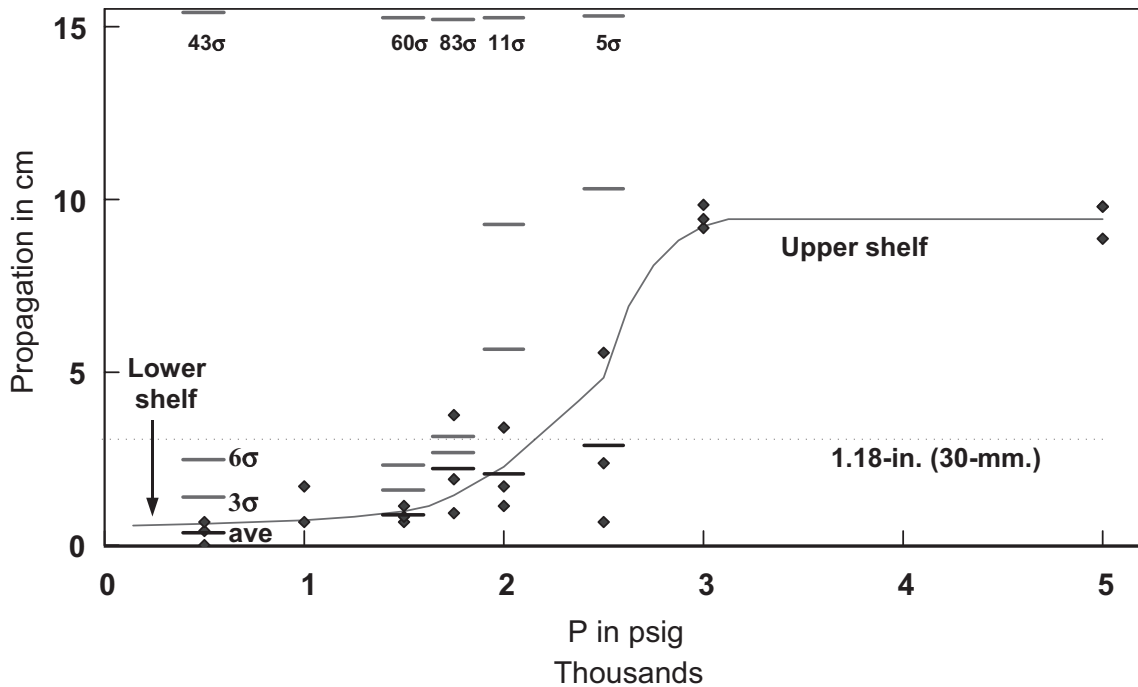


FIG. 5—Data from Zawierucha et al. [6] (their Fig. 5) for Hastelloy® C-276.

In some fire-limit testing, thresholds can be very sharp, indeed. Fire limits of gases often seem to be measured precisely (but also often are not nearly so). Oxygen indices of plastics are often measured to within tenths of a percent of oxygen. And even some metals tests have shown an apparently sharp threshold. If all metal behaviors were like this, the present controversy would be moot. For many metals, the threshold is fuzzy at best.

Perhaps the earliest and most detailed discussions of threshold fuzziness in the G-4 collegium which seems to support this thesis is that of Zawierucha, McIlroy, and Mazella [6]. This thesis quite reasonably posits that if one attempts to ignite a specimen that is either far into or far short of its fire thresholds, clear threshold results are likely.

Far short of the fire limit, one is likely to obtain negligible propagations beyond the zone of influence of the ignition-energy damage. Far over the fire limit one is likely to obtain the highest probability of complete combustions in every test, *but that highest probability may not be near 100%*. These extremes are called “upper” and “lower” shelf regions per Figure 5, which is patterned after Fig 5 from Zawierucha et al. In this case, Fig. 5 is inverted from Zawierucha et al’s paper and hence his lower shelf is shown as the upper shelf and his upper shelf is this figure’s lower shelf. However, as tests are conducted that are closer to the fire limit threshold, the chances of intermediate results and scatter grow. As one approaches the fire limit from either extreme the theory argues that small numbers of test results will often fall short of completeness and ultimately there is a band of results in which propagations of any length may obtain and in which (potentially random) scatter in the results is acknowledged.

Data in this transition zone are shown as the “S” shaped function of Fig. 5. This is most likely a best “eyeball” fit, but in principle, the transition curve is the average or some other statistical metric (mean, median, mode, etc.) of the results. As a result, one would expect a distri-

bution of results about the metric (the central tendency) for tests at each pressure.

In this case of Hastelloy® C-276 [6], the transition region (scatter) as a function of pressure appears to stretch from about 1000-3000 psig. And indeed if one takes the data on Fig. 5 from the 500, 1500, 1750, 2000 and 2500 psig levels (because three points can be discerned at each), assumes a normal (Gaussian) distribution (not necessarily so and possibly *not* appropriate) and calculates a mean and standard deviation for each, one obtains the results shown with the lowest bars (for the average) and higher bars for various sigma, σ , levels. Each (except for the 2500 psig point) exhibit the 3σ , and 6σ , points as well as the number of σ that would correspond to a propagation that would yield a complete 6-inch (15.2 cm) result taken as a complete combustion by standard G 124. In the case of 2500 psig, the six-inch point occurs at less than 6σ . These predict that at 500 psig, and 1500 psig, the probability of achieving a 1.18-in. (30-mm) propagation is at, or less, than the 3σ level and indeed, predict that to achieve a full 6-inch propagation would require testing to the 43σ , and 60σ levels. All incredibly unlikely.

In comparison, at 1750, 2000 and 2500 psig, one of each set of three tests has indeed produced a propagation exceeding the 30-mm threshold that Sparks et al. [4] propose for inferring that complete specimen combustion is likely and yet for a complete 6-in. combustion to be predicted by a normal distribution, testing would be required to the 83σ , 11σ and 5σ levels respectively, and all of these are still extremely low probabilities.

In actual oxygen systems, there are few recorded cases where ignition has resulted that did not yield extensive damage. That is to say there are few real-world experiments in which fires started and went out without significant propagation. One might argue that for one to consider Hastelloy® C-276 to be unacceptable for use at 2000 psig because one ignition with a probability at less the 11σ s level might be a self-sustaining fire is overly conservative, when there may be no incidents of either kind on record.

Again, the assumption of normality may be flawed and will be examined further in a future opinion. For now, clearly all of these data are skewed and, indeed, the nature of the combustion is that the further a specimen combusts the further it will tend to combust, so a Poisson distribution or perhaps other much-different distribution may be more applicable. But this most common statistical treatment suggests rates that are a real stretch.

Nonetheless, carrying this perhaps already-too-coarse analysis further, there are some who calculate the probability of all the air molecules in a ASTM G-4 meeting room statistically going into one corner leaving the members suffocating in a vacuum. Such an event can also happen in theory, but it does not happen often (not yet once in the writer's recollection) and like the data above, will only happen when results are many sigma from the mean, that is, many sigma from the normal meeting-room environment.

This may suggest there may even be four regions of interest instead of three. Fig 5 exhibits hypothetically how way below the threshold (lower shelf) the results all tended to be negligible, how far above the threshold (upper shelf) the results all tended more to complete combustion (but may not always be complete), but that between the two shelves there may be both a region in which some results are complete combustions and some are scatter, and yet another region in which the results are only scatter that never produce a significant chance of complete combustion that might be interpreted as indefinitely self-sustaining combustion.

The writer is not aware of dialog in the community as to what might be an acceptable sigma level at which to accept a low probability risk of self-sustaining combustion. However, it is perhaps worth suggesting that ignoring an outlier test result might be justified on the basis

that if only one out of ten, or fifty or one hundred ignitions in a system are self sustained, that they might not be realistic risks, provided in actual real-world oxygen systems there is significant experience in systems without a large number of accidental ignitions that failed to sustain combustion reported. Within the writer's knowledge, among the entire collection of oxygen systems in service regardless of severity and compatibility, there have been in total a few but apparently very few at that. Could they have been happening without being noticed?

To wit, Engel et al. [7] provide some recent (2006) data that add excellent insight. In this work a nonstandard 12 in.-long (305-mm-long) specimen of 347 stainless steel was used. These present the most stringent tests of self-sustaining combustion of relatively huge specimens the writer is aware of. Not only that, but there were a *lot* of tests performed at some conditions, surpassing the writer's own efforts in number. The paper reports that at 3.45 MPa (500 psia) there were 55 specimens tested; at 6.89 MPa (1000 psia) there were 41 specimens tested. And the results are illuminating.

Engel et al. [7] use these data and similar and remark:

- “Previous thinking was that below a certain threshold, no burning would occur and that at slightly higher pressure, the rod would be completely consumed” (Engel 1).
- “These data do not appear to correlate, and little or no pattern would emerge if significantly fewer data were obtained” (Engel 2).
- “A minimum ten samples is recommended to define the cumulative distribution for one temperature and pressure set”. (Engel 3)

Rebuttal 2

The writer acknowledges and appreciates many of these same data that have been supplied to him by one of the Engel et al. [7] paper's coauthors, Stephen Herald. There seem to be real gems of critical information in these bounteous data, but when wading into such voluminous statistical results, as when gambling in a casino, the words of Disreali, Twain and others (who may have said it first) come to mind: “There are lies, damned lies, and then there are statistics”. The problem with finding the 800 pound gorilla in this room is often that it is unfairly hiding behind the potted plants. This commentator, although not nearly a sophisticate at statistics, would like to take another look at these data and draw coarse conclusions from a different and contrary Devil's Advocate perspective.

The first conclusion (Engel 1) is a normal optimistic tendency of human nature to seek clarity and it is reinforced by all those materials that seem well-behaved, but it must be challenged. Although the body of work from Zaweriucha et al [6], including numerous additional papers over a decade or more, focuses on the “transition” region for variable concentrations of oxygen, the original recitation of the concept [6] includes an example of a wide transition region in its Figure 5, (used herein also as Fig. 5) and it does indeed also address the issue of two-dimensional variation of the transition as a function of both pressure and oxygen concentration in its three-dimensional plots for its Figs. 9 and 10. Indeed, the expectation of a sharp threshold is not a declaration in the original G 124 text and is actually disclaimed (e.g. Note 7 in G 124-95 mentions how erratic extinguishment and other intermediate results are prospects).

In the world of gas-phase combustion, fire limit data are usually plotted on a ternary diagram (or something like one) and the limit is established not through a mean but by drawing a

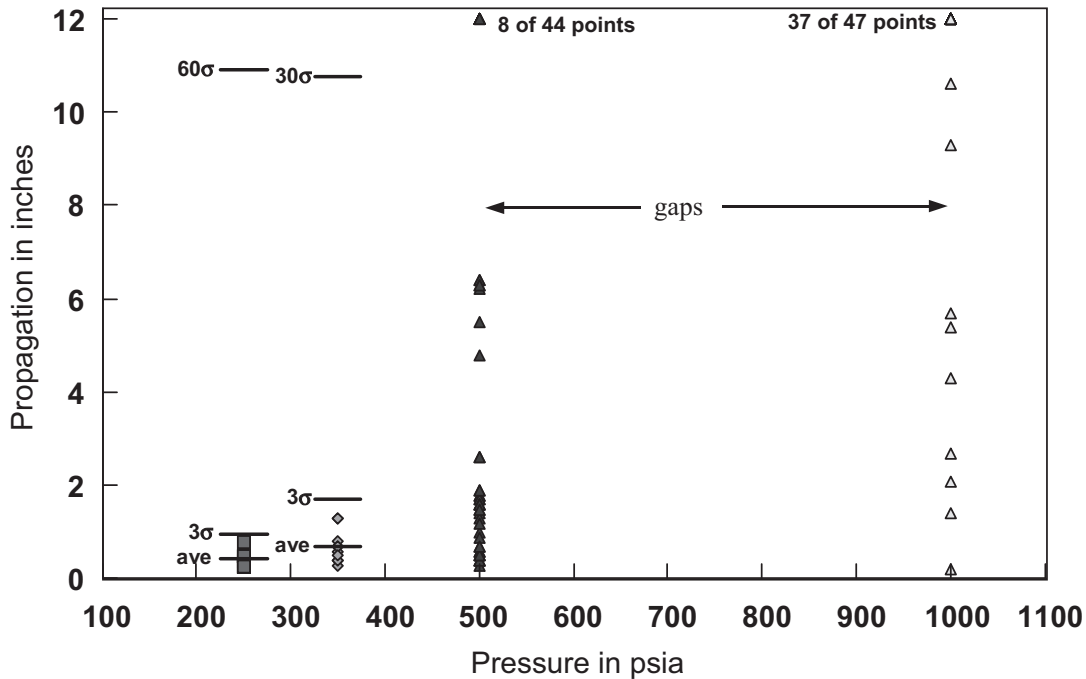


FIG. 6—Engel et al's [7] promoted combustion test results for 347 stainless steel.

line or curve through the extremal minimum complete combustion data points. On one side of the line there are no complete combustion points, but on the combustible side of the line there are typically numerous incomplete combustion points. Mean (average) combustion is not the parameter of interest nor is extremely low-probability complete combustion. In most testing, the knowledge of the boundary is at far less than the 80 sigma, or even six sigma level and less. At the risk of splitting hairs, the historical perspective might be said to have been that below a certain threshold no *self-sustained* burning would occur.

The second conclusion (Engel 2) seems to undersell the importance of his data runs. Although it does not stand out in his paper, and hides like that 800 pound gorilla, in Engel's Figure 3 (Fig. 6 as annotated herein), the 500 and 1000 psia runs may appear to be a scattering of transition-zone data with the random long and even complete combustions that seem to prove a significant propagation will ultimately lead to a complete combustion, *but if so, that is not at all the opinion of this observer.*

The number of these test data obtained for use here in Fig. 6 as of this writing (2010) do not correspond exactly with the data counts in the 2006 paper but are similar. They are plotted in the style of Engels' Figure 3, and exhibit similar behavior.

At the 500 psia test pressure, the complete combustion point (which may appear to be a random long propagation) actually represents *eight* of 44 specimen tests representing about eighteen percent of the tests. Similarly, at the 1000 psia test pressure, the complete combustion point actually represents about 37 of 47 specimen tests representing about 80% of the tests. If these data were normal (again which they may well not be), a *minimum* five specimen set of tests at 1000 psia would be expected to produce, "on average", 80% or four complete combustions, so that 1000 psia clearly would score at or above the threshold. A minimum five speci-

men set of tests at 500 psia would be expected to yield, “on average”, only “0.9” complete combustion results and it would require six specimen tests to expect a complete combustion, “on average”. However, since more than half the results would be expected to be greater than 30-mm (the proposed new threshold) this would serve as a red flag to the astute experimentalist to extend the number of tests. *And these are 12-in.-long specimens!*

As was done with Zawierucha et al.’s. [6] data, Fig. 6 also exhibits bars depicting the average propagation lengths and various sigma levels for those tests that did not produce a complete combustion result. At 250 psia, fourteen tests yielded a maximum propagation of 0.8-in. (24-mm) that is short of the 1.18-in (30-mm) criterion suggested by Sparks et al. [4] for inferring ultimate complete-combustion probability. The average propagation was 0.45-in. and the three sigma point is at 0.97-in. predicting a low probability of any specimen test occurring above this level (a normal probability of only 0.00135 or about one test in a thousand above the criterion). At 350 psia, eleven tests yielded only one result at 1.3-in. but this alone would rank this pressure above the new criterion and, therefore, score this pressure as above the threshold.

However, if both the 250 psia and 350 psia data are again viewed as normal (again, perhaps a flawed assumption), the usual treatment would predict the probability of observing a complete 12-inch propagation (assuming that defined self-sustaining combustion) at the respective pressures, as being outside the 60 sigma and 30 sigma levels, respectively. And even for shorter 6-in specimens would place the probability outside the approximate 30 and 15 sigma levels, respectively.

In the case of Engel’s Fig. 3, there is a clear lower shelf including 250 and 350 psia (of negligible combustion labeled “igniter effect”) that Engel designates at up to slightly below 500 psia, a clear upper shelf slightly above 1000 psia (that is nearly all complete combustions called “total burn”), and the region from slightly below 500 psia to slightly above 1000 psia (called “transition”) in which there is both scatter and complete combustion (which this writer, and perhaps Zawierucha, might score as part of the upper shelf based upon the discussion of Fig 6 here). However, if the 500 and 1000 psia results are taken as being above the threshold, then any transition region would be from somewhere between 250 psia and 350 psia to somewhere near 500 psia. Could this narrow band divide into two regions, one wherein there might be the onset of transient combustion with significant scatter but only a negligible probability of long propagation that might signal self sustaining combustion, and one wherein there is a realistic probability of long combustion that signals self sustaining combustion? Sparks et al. [4] admit that the adoption of their “markedly different” proposed 30-mm (1.18-in.) criterion would mean that the currently published thresholds for many materials “may no longer be defined” and they list in their Table 4, instances in which significantly lower thresholds may be measured. In the case of Engel et als’ data, that threshold is at or below 350 psia.

The forgoing discussion “seems” to bolster the third conclusion (Engel 3) in that for a ten set test at 500 psia, one would “on average” expect one or two complete combustions to score the pressure as being above the threshold. With the new criterion, about five tests would exceed the 30 mm criterion to score the pressure as being above the threshold.

But is that what these data should say?

Suppose one were to view Engel’s data as six inch specimens with a six-inch holder attached. Would the results differ greatly? Interestingly, the results using the six inch gage are nearly identical. For a ten set run of tests at 1000 psia, one would expect the previously cited

79% complete combustion rate for 12-in specimens and about 81% for six inch specimens, while in comparison the 30-mm results would be exactly the same for 6 or 12-in. specimens at about 95%.

In comparison, at 500 psia, one would expect the previously calculated 18% of specimens to propagate a full 12 inches, but 29% would be expected to propagate a full 6-in. In comparison, 70% of the specimens would exceed a 30-mm (1.18-in.) criterion.

All of the approaches, would indicate a significant probability of experiencing self-sustaining propagation following ignition of SS 347 at 500 psia or above. But there is disagreement among them as to whether to score 350 psia results as being above the threshold.

The issue is whether legitimate scatter between 350 psia and 500 psia is indicated or whether the threshold would-be closer to 350 psia than to 500 psia? The scoring of this band is not trivial since many industry applications are in this zone and a threshold of 500 psia might support the use of 347 SS in some cases, while a threshold of 350 psia might exclude it.

But in the spirit of the promised Devil's Advocacy, Engel et al's. data warrant further examination. Fig. 6 flags "gaps" in both the 500 psia and 1000 psia data. And Engel's Fig 3 exhibits similar gaps at other pressure levels also. Indeed, despite complexities that might intercede, one would "normally" expect a normal distribution to reflect a progressive gradient. There is a "central tendency" (typically mean) somewhere and the greatest density of results should be near that mean and the density should tail off in both directions. This is not what happens in Engel's 500 and 1000 psia data. There are clusters of results and large open spaces. And this might also suggest there are multiple distributions overlaid.

One possibility that the writer would consider is the presence of yet another transition (this time in the vertical direction) possibly due to some apparatus feature or specimen feature. If the distribution were normal, then one would expect to see data in the large open gaps indicated on Fig. 6. Instead, what one sees in both cases is that the results are scattered (without an obvious norm) up to a point (curiously at about 5-7-inches) but that any specimens that burned to that point, transitioned to a different burning mode and were then nearly always assured complete or near-complete combustion. They were then like analogous friction blocks sliding down hill at greater than the angle for the static coefficient of friction—their inclined plane suddenly bent downward (they dropped off a cliff). How can this be?

The writer speculates on this, because he has witnessed just such a phenomena in oxygen index testing of nonmetals, *and it may be pertinent*.

In the early days, OI testing involved some specimens that were ill behaved and had the tendency to drip sludge, crud and even molten metal into the glass bead bed below that mixes the incoming gases, creating a fire hazard in later tests of higher oxygen concentration and disrupting flow, and one enterprising tester placed a brass disk perforated with a series of holes over the glass beads. This caught the drippings and kept the glass beads clean. However, the glass beads also serve to redistribute flow, and the disk also resulted in the formation of a series of oxidant jets spraying upward towards the specimen, and in turn forming eddies, and recirculation of the gases. The glass beads provide mixing, but if not clogged by debris, they also provide a laminar gas flow.

Literally, the perforated plate caused a division of the turbulent oxidant flow at the mid point of the specimen with the flow at the specimen surface being upward over the upper half and downward over the lower half. If one were testing PTFE and ignited it timidly near its threshold, the preheated portion would burn with a decaying (note: visibly nonequilibrium combustion) flame and ultimately extinguish—a clear negative (not self-sustaining) result. How-

ever, with more robust ignition, a greater “push”, the flame would still decay (still nonequilibrium combustion) but it would take longer for the extinction to occur (even to the point at which it might achieve and exceed the time criterion for an inferred positive burn, even though it was still a clear negative, nonequilibrium combustion, result). However with sufficiently robust ignition (or if a shortened or repositioned specimen were re-ignited) the flame would again decay while the propagation advanced downward (yet again nonequilibrium combustion) until the flame found itself near extinction at the midpoint of the specimen at which place the weak flame would reverse direction, no longer diffusing upward and would be blown downward by the recirculation eddy. As a result, the flame then started to preheat the PTFE below and the flame would accelerate (now running symbolically and literally “downhill” at an increased angle of incline in the friction analogy, dropping off of a cliff). And as a result, any time the combustion got to the mid point it was assured to completely combust the specimen (even in concentrations much below the ultimately measured OI). There were two distributions clearly in effect.

Whether or not due to a similar mechanism, this is the same result reflected in the Engel 500 and 1000 psia data sets of Fig. 6. Once the combustion got to the approximate mid point of the specimen, complete combustion was nearly certain. Did it simply shift through the fire limit condition there? It suggests a careful examination of the apparatus is warranted to rule anything similar either in or out. Did combustion-induced flows reverse? Did the buoyant hot gases ultimately convectively preheat the upper specimen to facilitate late combustion, accumulating heat in the upper six inches? Did debris from the igniter deposit on just the first six inches (or alternatively just the last six inches) and inhibit early combustion until the fire got past the debris?

Indeed, Binder et al. [17] report on the effects of ceramic coatings interfering with combustion, and Engel’s igniter may just be depositing igniter chemistry (aluminum or palladium or magnesium or their oxide powders on the first six inches of the specimen)? Some of the lowest thresholds the writer has measured for steel combustion employed an igniter principally of steel (and a small amount of magnesium) that would interfere much less with the chemistry the way some dissimilar promoter materials might. The igniter metal of iron was rendered more flammable than the bulk specimen (as is required of igniters) by employing a series of staged, high surface-area-to-volume features (small diameter wires, leading to thin-wall tubing, and segmented prongs) to very gradually form the desired molten droplet at the rod tip with less intense fire and less differing chemistry [18].

There are many possibilities. Indeed, two specific possibilities deserve more extensive discussion here: pressure build up and carbon chemistry.

Pressure Buildup

G 124 is conducted with a sealed vessel, and during combustion, the system pressure likely experiences a surge during ignition (that might drop off) and then builds to a maximum (one of the indicia that combustion has ceased) and then decays and the initial and final pressures (but apparently not the peak pressures) are recorded. However, pressure buildup promotes combustion, elevates adiabatic combustion temperature and heat transfer from the combustion zone of the specimen and, in turn, combustion promotes pressure buildup, and so this is again a positive feedback situation that can also cross a threshold and lead to sudden runaway combustion. An initial spike in pressure during ignition is actually a form of enhanced ignition that like the preheat must run down. The two effects can compound each other. And in late-stage eleva-

tion of pressure, the final combustion may be significantly further across the fire limit than was the initial combustion. Indeed, G 124 reports the starting pressure as the measured result, but reporting the final pressure might be more valid (and conservative).

To avoid this exact concern, the writer has only tested with flowing systems that were limited (but not well-controlled) in pressure buildup by a back-pressure regulator. And indeed, the writer's waning recollections of his results were that they were statistically better behaved than for those from Zawierucha et al. [6] Engel et al. (7). Perhaps this was a factor (but maybe not the only one) in Engel's split distributions. In most real world incidents one would anticipate a constant initial pressure, rather than a constant volume, situation. However, oxygen safety practitioners may well need information to cope with both prospects.

Consequently one must ask if the igniter is not only pushing the combustion initially with its heat and chemistry but also with a transient pressure buildup? If so then the scatter in data may also be more so an artifact of the procedure rather than a property of the fire limit. Maybe it is the hardware or procedure rather than the criterion that needs adjustment. The writer recalls little reported in the literature about the transient pressure effects in G 124. Maybe study or reconsideration of the use of a sealed vessel is needed.

Carbon Chemistry

Some materials affect combustion even in small amounts. In the early 1990s, NASA reported a stunning effect that small variations in composition had on the threshold of nickel alloys [19]. However, metals are not the only potent additives. Carbon chemistry is another perhaps even more important effect, and yet such carbon effects are curiously controversial and seldom discussed in the G4 collegium.

In the mid 1980s NASA WSTF tested Alloy 440C (~1% C) and found its lowest propagation at up to 2500 psig, then decarburized it and found specimens (at 0.2% C) to propagate as low as 1000 psig. To the writer's knowledge, these results were apparently pursued no further and were not yet reported in G 94-92.

In the later 1980s, Zabrenski et al. [20], tested 304 stainless steel and found it to propagate at 725 psig, then purchased a second batch and found it resisted burning even at the 1500-psig pressure limit of their apparatus. Following a metallographic study of the two batches, the second batch was found to have very small grains and slip-lines exhibiting work-hardening, and upon annealing (which may have also altered the carbon content or carbon distribution), found it also burned much more easily at pressures at least as low as 875 psig.

In the mid 1990s the writer [21] found curious combustion behavior that conflicted with then-recent observations of large scale "excess oxygen" in burning steel and may well have been due to carbon presence. Lanyi [22] later examined the behavior of carbon in steel making and analyzed and defended the potency of carbon based on a wealth of Basic Oxygen Process steel industry data.

Since the latter 1990s and to this day [12], the writer has been, and remains, a strong proponent of more thorough study of the effects of carbon in metals especially in steels and was a proponent of including such study in the Industry Sponsored ASTM G4 Test Program 96-1 (but could not persuade other sponsors). Carbon has a clearly potent effect on flammability, even in small amounts and is variable in a way that is seldom documented, nor is it easy to document, with sufficient precision. It is also something that is easily adjustable within the existing technology and might allow for tailored or controlled flammability in numerous alloys

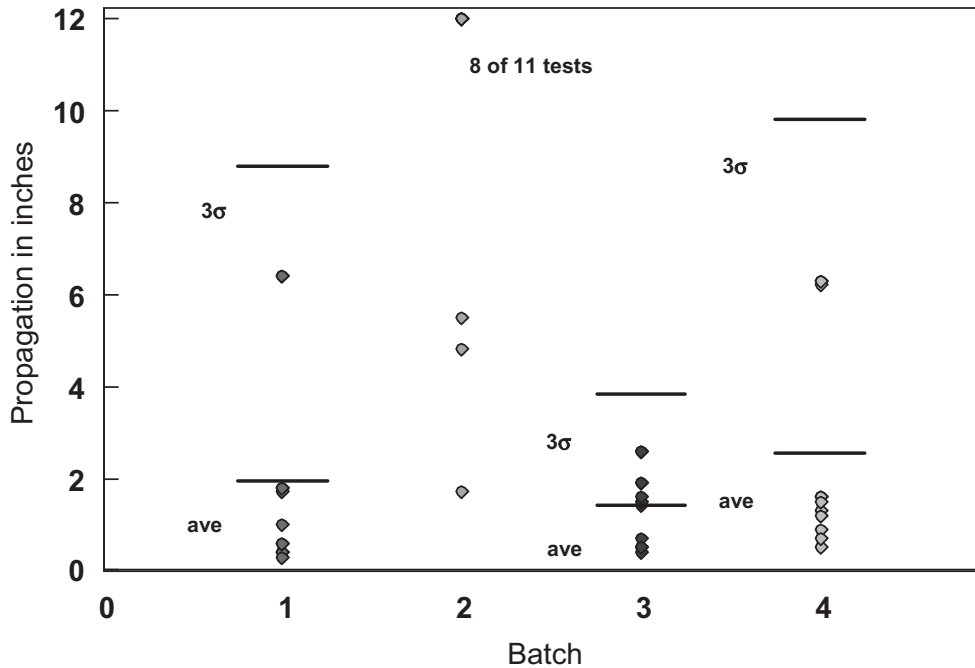


FIG. 7—Data from Engel et al. [7] for four batches of tests of stainless steel 347 at 500 psi.

that would allow for practical economic upgrading of compatibility. However, there is also strong opposition to this hypothesis that thwarts a definitive reconciliation, despite the good amount of reputable supporting background.

Carbon though combustible is a known potent inhibitor of iron combustion and as such, variations and random distributions from batch to batch and possibly even from specimen to specimen or from region to region within a specimen may just be a potential source of data scatter like that seen in Zawierucha [6] and Engel et al. [7]. If carbon were to be studied and if such an effect were validated and thereby vindicated, it might suggest decarburization of all tested alloys should be employed as a way to identify a more certain (and more conservative) base minimum threshold for steel alloys, as well as might suggest a criteria for those who might wish to use carbon as a “fire-proofing additive”.

Nonetheless, as of this writing, the role of carbon is largely ignored by the oxygen safety community and many alloys are being treated identically, despite these data and the potential for enormous *relative* variations in the amount of carbon they may contain.

A Last Statistical Notion

In view of the mechanistic suggestions above, a return to the statistical approach for examining some of Engel et al.’s data is warranted. The data of Figure 6 appear to clearly imply the threshold pressure for self-sustaining combustion of SS 347 is no higher than 500 psig. But consider Figure 7. Figure 7 is based on the data provided to the writer for 500 psia tests of this alloy. The data appear to have been collected into four batches as shown. Might these batches

indicate different testing days, specimens from different batches of alloy, specimens from different rods of the alloy, etc.? When the “batch” results (in the writer’s possession) for the 44 specimens tested are presented individually a different picture may be suggested.

Notice that for batches 1, 3, and 4, that there is *no* complete combustion result recorded. And if the averages and standard deviations are calculated for these eleven-specimen runs, the results are all pretty similar. Average propagations are in the vicinity of 2-in. and the three sigma points for batches 1 and 4 are at about 9-in. while the 3 sigma point for Batch 3 is somewhat less at about 4-in. All three of these would score the 500 psia level above the threshold if interpreted with a 30-mm criterion. And yet these three runs, indicate the probability of even one complete combustion are at no less than the 4 sigma level (meaning a probability less than 0.0000317, or no more than one complete combustion in more than 30 thousand tests). And yet the second batch produced complete combustions at ostensibly the same conditions at a rate of 8 out of eleven tests, and *all eleven tests results were at or above the average for the other three sets*.

These may be a valid statistical fluke. Maybe batch two was just highly improbable, like tossing eight heads in eleven coin tosses. It can happen. But when it happens in just four batches of tests, it runs up a red flag for there being an unidentified variable present. If indeed, the second batch of tests is an outlier (since that is more likely than the other three batches being outliers), it again calls for reconsideration of variations in the apparatus, procedure, and/or the specimens as causal features.

Hence, perhaps SS347 is, or could be, a much more compatible alloy than these composite data might suggest.

Is that finally it? Closing Discussion

There are good reasons why some data sets that exhibit incomplete yet long-propagation results may indeed indicate a condition that is over the fire-limit threshold and will exhibit either equilibrium or accelerating combustion prior to extinction. But this writer asserts that there are scenarios in which certain kinds of specimens can be studied essentially extensively (“forever?”) with occasional and even frequent long propagations but without ever observing a complete combustion, and it is likely most, if not all, of the latter kind will *not* exhibit equilibrium combustion. The arbiter in standard gas phase fire-limit tests, in OI tests, and in the spirit of the original G 124 standard is whether the combustion is in thermal equilibrium that is crucial to self-sustained combustion at the limit. Allowing an inference to be drawn (as in the case of the current revision to G 124) that any incomplete combustion result proves the result is over the fire limit (in the absence of data about the equilibrium of the combustion) may rank some metals below the level they deserve, and while this is conservative for that particular metal (since it lowers its ranking), the upshot is not conservative if it results in the deployment of less fire-resistant metals that test better (less conservatively) because, but only because, they test differently.

The primary goal of much metal testing is to see if a metal will sustain propagation. Sustained combustion is what causes big and nasty incidents. Clearly one can conspire to optimize conditions and force combustion, and if any such scenarios like that were to be identified in practical hardware, then they warrant consideration. Still in traditional fire limit practice such issues have been dealt with through the application of safety margins and safety factors (and the oxygen safety community would be served well if a standard on margins and factors could be

developed).

Indeed, if such a standard or community practice could suggest that the probability of a complete combustion should be less than some sigma level, then the body of specimen tests at any pressure level could all be factored into establishing a threshold pressure (whether using normal statistical distributions or other more applicable distributions) rather than relying on potential outlier results. Some effort to this end are underway and this writer hopes to weigh in also in a later paper.

However, there can also be value to the measurement of where the onset of even transient combustion is located (as opposed to where combustion goes “critical”). That is to say data for where the “S” curve starts in Figs. 5 and 6 can indeed be useful (and might also be assigned on the basis of a sigma level) even if the combustion that results between it and any self-sustaining threshold only indicates the onset possibility of “fire caps”. While a fire cap may not be nearly as great a dread as a massive fire, it could be every bit as important to someone who was in or too-near the transient combustion zone.

Nonetheless, there can be a difference between the onset of transient combustion and the level at which the combustion for some metals goes “critical” and may sustain indefinitely, even if for some metals both boundaries occur at virtually the same point.

Statistical approaches aside, the best inference of self-sustaining combustion might be best made with close observation for equilibrium combustion when that becomes technologically possible and practical.

Conclusions

- Scatter in some tests by G 124 may be due to a “normal-like” statistical distribution from which a reasonably-probable complete combustion result may ultimately be predictable, but other test results may also be due to an igniter push (among other variables like anisotropy) that will assuredly run-down. Extrapolating to a complete combustion result is not valid without adoption of an acceptable-risk parameter.
- The specimen preheating due to the standard igniters used for G 124 may not initially conduct heat more than 30-mm (1.18 in.) along a test specimen, but this is not the only nor the full extent of any affects that ignition may produce.
- Ignition can produce pass-through preheating, can introduce catalytic or inhibitor materials to the specimen, to the molten tip or can produce deposits along a specimen’s surface that may affect droplet behavior for several inches or more along a specimen.
- Self-sustained combustion is dependent on many mechanisms and one key example is equilibrium combustion that has been central to many kinds of fire-limit testing and applications. Self-sustained combustion leads to the most severe incidents.
- Complete specimen combustion and similarly timed combustion have served well as indicators of inferred self-sustained combustion in the Oxygen Index tests, D 2863 and G 125, but there have been exceptional cases in which too-

slavish adherence to the criteria have yielded clearly false results.

- Complete specimen combustion has been an indirect method to surmise when equilibrium combustion, therefore self-sustained combustion, has happened in systems like that of G 124 that have not allowed for close observation. There is good reason to infer that this measure of self-sustained combustion can be flawed in exceptional cases.
- Drawing an inference that a specimen which propagates 30 mm (1.18 in.) or more implies that a sufficiently long test series would produce a complete combustion and therefore reflect self-sustained combustion can be wrong.
- Sorting statistical erratic extinction from transient combustion is best dealt with in Oxygen Index tests by examining the degree of equilibrium of the combustion rather than the time or extent of propagation and is likely the preferred approach to use with the G 124 test as well, if/when current technology will allow.
- When current technology will not allow assessment of equilibrium combustion, the ubiquitous use of personal computers and software, such as spread sheets, today allows for mundane (as in this writing) or more sophisticated real-time statistical assessment of the standard deviations or related measures to assess whether the probability of complete combustion is a concern, provided guidance as to valid risk levels is provided.
- Agreement is needed as to how improbable complete combustion results should be, and consensus software algorithms or spreadsheet macros can facilitate that assessment.
- Measurement and reporting of the threshold for transient combustion, or combustion/scatter onset, is useful data and may warrant measurement but is not appropriate in this commentator's mind for substitution as historical fire limits.
- Validation of a long-but-incomplete propagation result as reflective of the fire limit may require as a minimum the exploration of scatter results under close observation (for example the study of metals at low pressures in glass vessels, etc.).
- The role of pressure, carbon, and other properties, including statistical treatments of data, for the G 124 standard warrant study.

Summary

ASTM Standard G 124 may publish with new positive test criteria in 2010 or thereabouts as a consensus standard, but it is not without the solitary dissent and protest registered

here. This commentary has disagreed with the new fire-limit definition and the bases have been reviewed in detail. Both the experimental efforts to measure the maximum reach of igniter effects and the idea of a statistical approach (as presently presented) have been disputed. Alternatives have been suggested.

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Barry L. Werley¹

A Challenge to the Fitness-for-Use of Standard G 124-10 to Select Metals for Oxygen Service

REFERENCE: Werley, B. L., “A Challenge to the Fitness-for-Use of Standard G 124-10 to Select Metals for Oxygen Service”, Self-published opinion, 2014, public domain 2020, 15 pages.

ABSTRACT: A revision of the positive-burn criterion of ASTM G 124 in 2010 marked a change viewed by many as an obvious much-needed long-overdue evolution but viewed by the writer as a revolutionary, unjustified change that renders the standard unfit for use, and potentially difficult to defend in litigation. The bases for this assertion are presented as an effort parallel to a related appeal to the ASTM Committee on Technical Committee Operations (COTCO) for a revision of the ASTM Regulations.

KEY WORDS: criterion, promoted combustion, ignition, self-sustained combustion, fitness, strict liability.

An automobile runs into a crowd and the driver of the car claims innocence, because he had taken his foot *off* of the accelerator pedal *before* the car hit anything. He was therefore no longer adding energy to the car and its further motions were therefore independent of driver input. Or *was* it? An oxygen system burns a user, and in court, a defendant denies fault because the system was designed with consensus ASTM standards specifically G 124-10 for *Determining the Combustion Behavior of Metallic Materials in Oxygen-Enriched Atmospheres* and was therefore made of the most compatible of practical materials. Or *was* it?

ASTM Committees like G-4 on Compatibility and Sensitivity of Materials in Oxygen-Enriched Atmospheres forge consensus standards in the blast furnace that is ASTM’s ballot process. However, the robustness of the consensus for every standard thus forged is not always the same. Some standards have a unanimous consensus. But standards can issue with an official consensus for which there can be significant protest and dissent. At present one can not tell these standards apart. ASTM G 124-10 is among those with strong dissent.

ASTM G 124-10 was revised in 2010, and the writer considers this most recent version unfit for use. Nonetheless, it was forged in conformance with current applicable ASTM Regulations. Therefore, changes to the ASTM regulations are being proposed to the ASTM Committee on Technical Committee Operations (COTCO) that allege the current regulations allow standards to publish with a “consensus” that is far too flimsy to be called a real consensus for life-or-death safety work, and that the current regulations also allow the level and extent of dissent and protest that may exist to be obscured, even to some members of the asserted consensus, itself.

Nonetheless, G-4 was not forced to publish with what is alleged here to be not only a

¹No mailing address. This paper was prepared for self-publication and archiving on a CDRom [REDACTED].

flimsy but a wrongful consensus. If this solitary allegation is correct, was this a too-earnest inadvertent result of an effort to make progress or was it an exercise in working around the spirit and intent of the system? The correct branch of this dichotomy is not known. Hence, whether the appeal to COTCO prevails or not, this paper is intended to suggest G4 apply a more collegial and transparent approach to its standards development, and perhaps more importantly it will contradict the technical basis for this particular revision on behalf of consumers who may not be aware of the controversy but may confront the oxygen hazard.

ASTM is a Society that claims it welcomes participation by all. A criticism of a standard by a nonmember of the Committee with jurisdiction must be treated with the same rigor that a negative ballot from a charter member would receive. ASTM G-4 is not a classified Committee (a Committee with such a lopsided participation by some interest group that it alone can sway, or even dictate balloting), however, much to the opposite, while there is at least some representation (that is fairly balanced) from oxygen suppliers, and vendors, and related standards groups and government groups, G-4 appears devoid of representation from consumers. Consumer protest is more likely to be found in the filing of litigation. Hence this paper is not intended to re-litigate the ballot proceedings that revised G 124, because the writer's opinions and arguments are amply presented in the many extensive negative ballots and supporting analyses, [*1,2*]² that have been supplied to the Committee before and after the recent revision and numerous previous ballots. Rather this is to illuminate the issue for those who did not participate in the decision, including consumers and non-attending G-4 members who may or may not need to challenge the suitability of hardware that may have injured them. And it alerts those who may need to defend this procedure.

To do this, the following elements will be presented.

- A statement of the controversy.
- A history of the development of G 124 from the protester's perspective.
- A citation of the two principal arguments for the revision.
- An explanation of why both arguments are being contradicted.
- A layman's opinion of how these arguments might impact litigation.

A Statement of the Controversy

ASTM G 124 measures the values of parameters that can affect flammability of metals. It has been used to explore the role of pressure, and temperature, and geometry but can also be used to study oxygen concentration and other parameters, at which a specimen will just exhibit self-sustained combustion, meaning combustion without external stimulus (that is, externally sustained combustion). It does this by specifying a procedure to test numerous rods by igniting them at their bottom and scoring where the transition occurs between those that were flammable (which "burned") and those which are not (which did not sustain burning). These threshold data are used primarily to rank the suitability of metals for service, but also to set acceptable service (exposure) limits.

Between 1994 and 2010, the threshold was based on where the minimum condition at which complete or nearly complete combustion occurred and specimens that did not burn completely even if they did exhibit appreciable combustion were scored as being below the threshold. This is the way combustion is scored in flammability-limit testing of gases and nonmetallic rods. The 2010 revision of G 124 substituted a 30-mm-specimen-burn-length

²Italic numbers in brackets refer to the reference list at the end of the paper.

criterion as being above the threshold and signifying self-sustained combustion.

History of the Development of G 124

In the early 1980s, NASA's White Sands Test Facility (WSTF) launched an effort to find test methods more suited to evaluate certain materials than their historically used LOX mechanical impact test (ASTM D 2512), specifically for metals. They started a series of meetings referred to as an RTOP (a Research Technical Operation Plan) and invited numerous government and industry members to participate (the writer was among them).

Every test method in use was tabulated and examined and new alternatives were suggested. Among the most popular candidates was the ASTM Oxygen Index Test which had already been adopted by some companies for evaluating nonmetallic materials, and had been adopted by ASTM Committee G-4 for that purpose, and was being explored in various configurations for broader use with metals [3-5]. The Oxygen Index test was first published within ASTM Committee D 20 on Plastics in 1970 as a test for polymers akin to those used to measure fire limits of flammable gases, and was directly related to the minimum-oxygen-for-combustion fire-limit of gases.

NASA's first efforts were aimed to measure metal burn velocities, "burn rates" [6], but the apparatus in this procedure was quickly employed to conduct multiple tests akin to those used in the oxygen-index procedure to identify thresholds in pressure and temperature that rank metals the way the oxygen index ranked plastics.³ After multiple tests exhibited coarse thresholds (reporting the highest non-propagating pressures), data to be collected this way were commissioned at NASA WSTF by industry sponsors (Reported by Cronk [7] and Stoltzfus [8] in 1987) and used to support the first edition of ASTM G 94 on Evaluating Metals for Oxygen Service in 1987).

ASTM G4's Fourth International Symposium in 1989 produced more than a half-dozen papers from numerous sources relating to metal flammability, including numerous versions in which metal rods and the WSTF vessel design were used to establish thresholds. A draft standard based on the NASA vessel and procedure was begun in the early 1990s, designated G 124, and the first version was finally adopted in 1994.

The first ballots were controversial in that the first ballots proposed using an incomplete (but significant) propagation burn length criterion to indicate when the test conditions were *above* the flammable limit (rather than short burns to prove they were *below*). Negative ballots from the writer were among the controversy. The first published version used complete combustion as proof of being above the threshold. Nearly simultaneously, G-4 developed a variation of the oxygen index test, designated *G 125 Measuring Liquid and Solid Material Fire Limits in Gaseous Oxidants*, that allowed use of the oxygen-index method in configurations that *D 2863 Measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion of Plastics (Oxygen Index)* did not address, and to be applied to metals, liquids, granules, non plastic materials, etc. It also elaborated on interpretations of limit criteria, based upon the fire limit being established as the boundary at which equilibrium combustion

³ In the Oxygen Index test a specimen is top ignited in an upwardly flowing gas stream so that combustion products and heat are carried away from the specimen while in these tests, and others underway at the time, the specimens were bottom ignited to allow molten metal products to drop off of the specimen, but gaseous products still could convect upward along the specimen in both the stagnant NASA system and others that employed a flowing oxidant supply. Although there are plastics that melt when they burn and can run down the specimen and complicate standard-test results, they are few.

is just possible as is the cited foundation of oxygen index testing and flammability-limit testing in general and was the basis for the first complete combustion criterion in G 94.

However, in the years since first adoption, a strong core of support has remained for adopting a significant minimum propagation as an equivalent alternative to a complete combustion criterion, with the most recently revised ballots in approximately 2002, 2005, 2009, and perhaps other times. The writer consistently voted negative on each of these ballots and provided lengthy bases and even a detailed analysis (“**Drawing the Line on Fire Limits**”) in 2002 [1]. However, there were other negatives for other reasons cast as well, and because each of these ballots was withdrawn, ASTM procedures did not require any of these negatives to be addressed. And indeed, each succeeding ballot ignored the writer’s prior negative responses and continued to resubmit the proposed change of criterion.

The 2010 ballot was issued with a rationale statement which did not flag the previous dissent: “The reason for the revision is for the five year review release. While doing this review the Committee chose to include some long overdue changes based on the current level of understanding of the state of the art in metals combustion testing.” Nor did the text within the standard discuss the controversy to the change in criteria. The ballot drew one negative (the writer’s) at the Sub- and Main-Committee level, with 22 affirmative of 29 returned ballots out of 39 eligible at the Sub- level and 33 affirmative of 41 returned ballots out of 53 eligible to vote at the Main- level. Several dozen G4 members were of nonvoting status.

During the ballot review, the writer was asked to withdraw his negative based upon a recent publication: “**Determination of Burn Criterion for Promoted Combustion Testing**” [9] that claims to prove a 30-mm burn length “ensures all metals that burn a distance greater than 30-mm (1.18 in.) are burning independently of any promoter effects that preheated the test sample during the ignition process” and were therefore self-sustaining. A copy of the paper was provided to the writer who declined withdrawal, citing several preliminary concerns about the paper.⁴

In committee, the negative was reconciled by summarizing the writer’s demur in two ways “(1) no ballot rationale, and (2) disagreement over definitions of flammability and criteria for positive burns”. A motion offered that:

1. “...a ballot rationale was included relative to revisions to capture changing technology in metals combustion testing.”

2. The previously cited recent paper [9] was again cited to defend the change, a specific mention of research that found igniter chemistry perhaps as much as four inches above the igniter was countered with “The committee is not aware of any published research showing igniter chemistry above 30-mm.”, the writer’s argument regarding historical reliance on equilibrium combustion to define fire limits was countered with

⁴ Peer review procedures within ASTM and G4 have been rather uneven over the years. In the past controversial papers by the writer have been sent for peer review to those commentators most likely to find faults and indeed, on two occasions the obstinacy succeeded in censoring one of the writer’s papers and encumbering a second one, leading him to conclude the process was corrupt and withdrawing from further publication within the G4 “collegia”, however in this case, although the writer was invited to peer review several papers for this symposium, this paper was not among them., thereby denying its authors the commentary presented here. Although as a subscriber to no-fault publication, the writer would not have rejected the paper for publication, its sweeping claims would have not been allowed without qualification for the reasons cited here.

“Committee is unsure of a method to compare the two standards G 124 and G 125 (oxygen index)” [the genetic precursor to G 124], and finally with regard to the impact of the change in definitions without guidance: “Regarding the impact of introducing a new burn criteria, the committee is aware of the differences of this new standard and the impact it may have. The committee suggested the industry has already been using such a criteria for many years...”

“A motion was made to find the negative vote Not Persuasive. The motion passed:” The vote was:

Subcommittee For 6, Against 0, Abstain 1.
Main committee For 10, Against 0, Abstain 1.

Principal Bases for the Revision.

The writer is aware of two principal bases for the change in the criterion: (1) publication of the then-recent experimentation that asserted the new criterion was valid and (2) argument that any errors the new criterion would produce are on the low side and are therefore conservative. The writer is not aware of any obscure other bases that might exist.

Basis 1: The Recent Publication

In 2009 the Twelfth International Symposium on Compatibility and Sensitivity of Materials was held and the paper: “**Determination of Burn Criteria for Promoted Combustion Testing**” [9] was presented and published on-line in September 2009 and in the symposium proceedings (ASTM STP 1522) the following year.

The paper reported on experimentation that sought to measure the amount of preheating that occurs during ignition of a test specimen. The actual experimentation was impressive. Fast response thermocouples were located along a specimen and then a promoter attached to the bottom of the rod was ignited. Such measurements with hair-like thermocouples are very challenging to make and yet a fully credible set of measurements was reported.

The ignition model and rationale used to design the experiment is reflected in quotes from various parts of the paper in Table 1. The sequence of steps during a test represented by these quotations is depicted in Figure 1.

Figure 1 shows seven points in time, t_{1-7} , such that at time t_1 , a promoter is shown attached to a specimen (in this case most often a copper rod was used to maximize conductive heat transfer). Time, t_2 , shows the promoter ignited and its molten droplet forming at the bottom of the rod. Time, t_3 , shows heat from the burning promoter transferring into the rod above forming a growing heat affected zone (HAZ). Time, t_4 , exhibits the definition of the “event duration” as the time just as the droplet releases and “terminates” further heat transfer to the rod⁵. Since “...metals are more flammable at elevated temperatures” [quotation 2 of

⁵ This is akin to the time when a driver lifts his foot off of the accelerator pedal and “terminates” further addition of momentum to a vehicle’s motion. The writer rejects the precept that heat input from the promoter thereby ceases and has cited in the document he prepared in support of his 2001 ballot and in the email dialog following the 2010 negative ballot, that not all of the promoter can be assumed to drain from the rod, and that XRD analysis from droplets on test specimens that stopped burning perhaps four inches above the ignition point has found promoter metals. These data were rejected on the basis that: “The Committee is not aware of any published research showing igniter chemistry above 30-mm.”

TABLE 1 — Ignition Model

1. “When a promoter is ignited, a portion of the rod is heated beyond the location of the promoter.” “This heating is termed sample preheating”
2. “...metals are more flammable at elevated temperatures.”
3. “Testing was...to determine the distance that the promoter heats the metal rod prior to molten drops forming.”
4. “The distance heated by the promoter just prior to promoter detachment or consumption is referred to as the promoter heat affected zone (HAZ).”
5. “Burning was observed via high-speed video which was used to establish the event duration between the ignition of the promoter and the time the initial molten metal drop separated for the sample or was consumed.”
6. “Since no appreciable energy was added to the sample after the end of the event duration, it was assumed that sample would ignite and begin burning or quench and solidify after this event.”
7. “The event duration is thus considered the controlling time used when assessing the temperature data from the thermocouples.”
8. “...for several 300-series stainless steels, samples heated to 260°C (500°F) and below show little or no variation in flammability when compared to ambient temperature testing.
9. “Therefore, 260°C (500°F) was chosen as a reasonable temperature to use to determine what length of the sample was within the HAZ”
10. “...all metals that burn a distance greater than 30 mm (1.18 in.) [a statistically determined maximum HAZ] are burning independently of any promoter effects that preheated the test sample during the ignition process.”

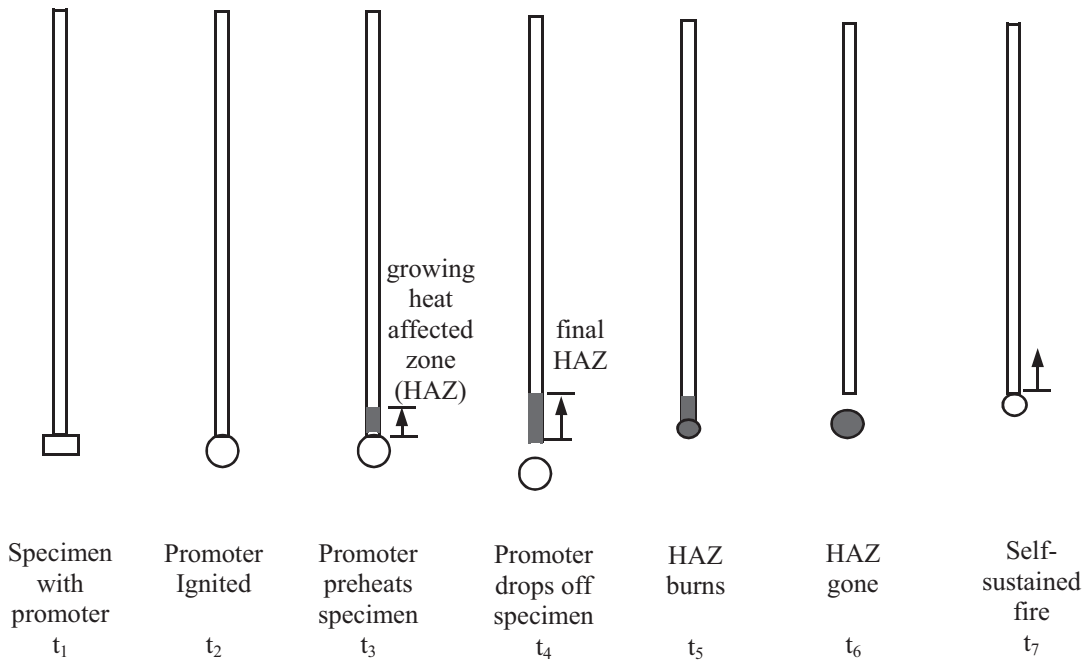


Fig. 1—Sequence of steps in testing model of Table 1.

Table 1] any burning of metal at time, t_5 , in this preheated zone is not considered self-sustained. At time, t_6 , the preheated materials from the HAZ are shown dropping off [not necessarily at the exact boundary as shown]. At t_7 , any combustion beyond the HAZ is considered self-sustaining, and indeed the paper estimates a statistical maximum HAZ for copper and adds a 50% safety factor to defend calling any combustion beyond 30-mm self-

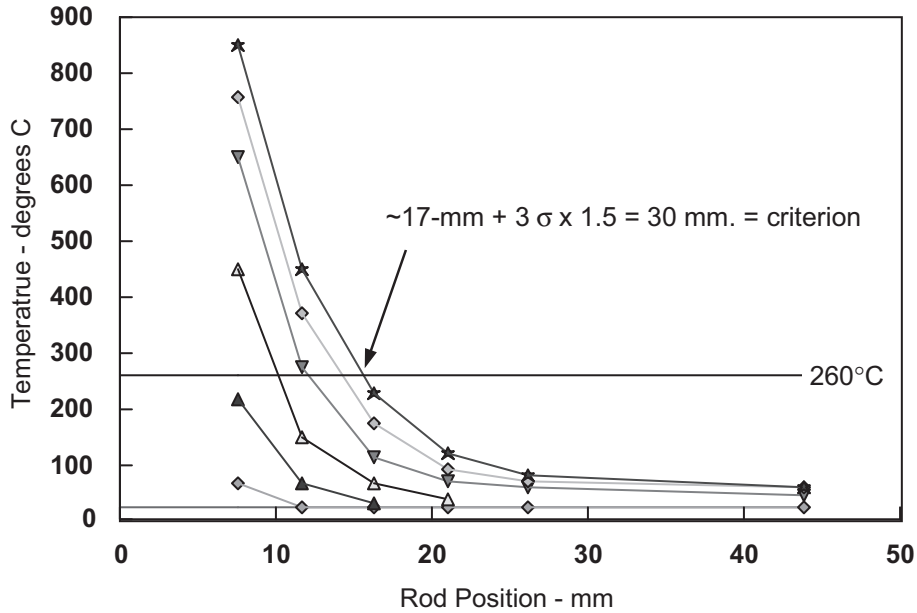


Fig. 2—A replot of data from Ref[9], Fig. 5 for temperature versus position for 0-0.6 s.

sustaining.

However, the HAZ end point is not something one can readily see. Heat flow does not usually have a sharp boundary to optically witness. Higher heat flow and temperature are “seen” closer to the igniter, and lower temperatures and heat flows are “seen” further from the igniter. Indeed, Figure 2 exhibits data from the paper’s Figure 5, re-plotted with temperature as a function of time for various distances from the igniter, rather than as temperature as a function of time for various positions.

The highest temperature curve shown is for the time just after the event duration time, and it clearly shows that the temperature in the rod is elevated at distances far beyond the 30 mm point. However, the paper’s ignition model in Table 1, offers two premises, quotes 8 and 9, that assert that several stainless steels showed no change in flammability⁶ when heated to 260°C, hence “260°C (500°F) was chosen as a reasonable temperature to use to determine what length of the sample was within the HAZ”. Therefore, Figure 2 shows a horizontal line drawn at 260°C and it intersects the curve at the event duration point (at about 17 mm). Adding three sigma plus a 50% safety margin yielded a 30-mm length and is the basis for asserting “...all metals that burn a distance greater than 30 mm (1.18 in.) [the statistically determined maximum HAZ] are burning independently of any promoter effects that preheated the test sample during the ignition process”.

Basis 2: The Fall-Back

Although the new criterion has been introduced into G 124, with no fan-fare, it has

⁶ The paper [9] does not state how this conclusion was determined. This might mean that the various alloys exhibited the same threshold and for stainless steels the Suggested Schedule of Test Pressures would put the results at 300, 500 or 1000 psig, meaning that the temperature might have changed the threshold up to 200 (500-300 psig) or 500 psig (500-1000). Of course the margin of change may have been measured to much smaller differentials also.

been admitted that use of the new criterion is going to produce at least some results differing from those previously achieved with the old criterion. However, in each case, the new threshold must by definition be at a lower (less severe) level and therefore *will* be conservative.

Disputing Both Arguments

Disputing Basis 1: The Recent Publication

The writer does not accept the model implicit in Table 1 when it concludes the entire promoter drops from the specimen at the event duration time, nor that 260°C is sufficiently low that this amount of preheat would not affect the fire limit of all metals of interest. However, the principal contradiction offered to this model here is its assumption that any propagation beyond the determined HAZ must be self-sustained combustion and, therefore, defines a positive test result.

The basis for this contradiction is exhibited in Figure 3. Figure 3, begins at the point on Figure 1 [t₄] where the promoter droplet has just fallen off leaving behind a heat-affected zone. The existence of a heat-affected zone is not unusual. Most, perhaps all, specimens that burn in a drop-wise fashion exhibit heat-affected zones after *every* combustion droplet detaches.

The significance of this first heat affected zone, HAZ₁, is that it was produced from the combustion of materials that burn more easily, burn at higher temperatures, burn fast, and/or otherwise facilitate the formation of a HAZ that is longer and hotter than an ordinary HAZ. Normal combustion droplets burning right at the fire limit under equilibrium combustion will produce a shorter, cooler, less flammable droplet than will the igniter and so the heat-affected zones they produce will also be shorter and of lower temperature.

The model of Figure 1 assumes that since the first preheated zone is hotter and longer than a normal equilibrium combustion zone that would be produced after a routine combustion droplet detachment at the threshold condition, then it is by premise [quote 2] more flammable than the normal-threshold combustion and so must be allowed to burn away before self-sustained combustion can obtain.

However, this is the rub. This admission of the HAZ being more preheated than normal is in fact proof that the HAZ provides a second stage⁷ to the ignition process. When the nichrome wire is flashed (which may itself be viewed as a first stage in the igniter), the ignition process is not over, because the wire ignites the magnesium or aluminum or other metal promoter (as a second stage), and similarly when that drops off, the ignition process is still not over if the preheated zone is more flammable than for normal (equilibrium) combustion *at* the precise threshold. It may be more flammable because it is hotter and longer or because it still contains reacting igniter materials or for still other reasons. Indeed, Fig 3 exhibits how the instant the promoter drops off of the first heat-affected zone, HAZ₁, its combustion by virtue of its greater enthalpy, can transfer heat into a second stage HAZ₂ that may be at a lower temperature or enthalpy than HAZ₁, and yet may still be hotter or have more enthalpy

⁷ In the old days when the Saturn Five rocket launched to the moon, a humongous first stage with humongous power, and energy lifted the capsule and then dropped off and a second less powerful stage kicked in to sustain the launch, and later a third stage was used.

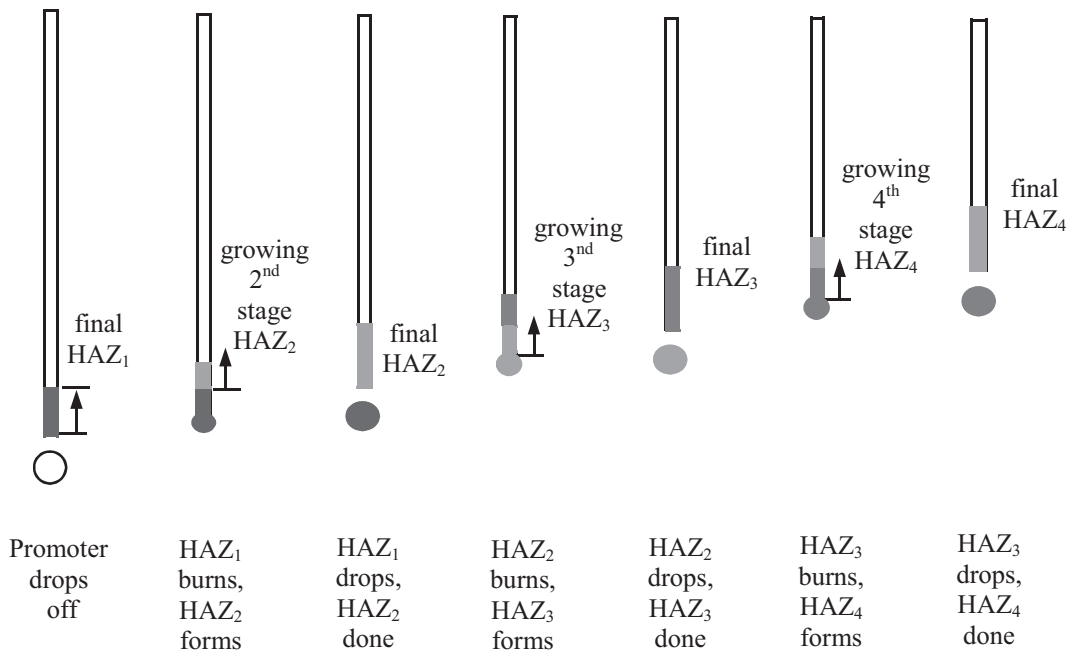


Fig. 3—Model that factors in equilibrium combustion concepts ala G 125.

than would be present during equilibrium combustion after an equilibrium combustion droplet detaches. And there may be a HAZ₃ and HAZ₄ and more stages until at the some point, x, the HAZ_x is settled into equilibrium.

If at any point the loses at some droplet produce a HAZ below the equilibrium combustion stage, extinction occurs.

Figure 4 exhibits an approximate thermo-chemical equilibrium scenario for iron combustion as has been presented in the past [10]. The solid middle curve is the enthalpy versus temperature curve for iron, the dashed curve to its right is for iron plus sufficient heated oxygen to produce hematite. The upper solid curve is the enthalpy versus temperature curve for wustite (plus sufficient oxygen to produce its complete combustion to hematite).

If the initial preheat zone (HAZ₁) is equivalent to a composite average preheat from point, A₀, to point, A₁, and if adiabatic batch combustion occurs it would heat the resulting products to point B₁. If for the sake of argument, we assume all droplets are the same size and detach at 2500 K (which is probably not correct either in the temperature or the assumption all droplets detach at the same temperature or are the same size) then when the droplet is ready to fall, an enthalpy equivalent to the heat, H₁, could be transferred to form a second HAZ₂, and more than half that heat could be lost to the ambient and yet still yield the average equivalent temperature of HAZ₂ at point A₂. If the HAZ₂ adiabatically batch combusts, it shifts to point B₂ which upon cooling to 2500 K would be able to transfer heat to form a third HAZ₃ and more than half that heat could also be lost and yet still be able to produce an equivalent average temperature to achieve an average HAZ₃ condition at point A₃. In turn A₃ can adiabatically combust to point B₃ which can transfer a heat H₃. If after heat loses, H₃ produces a HAZ₄ at point A₄, then things can change.

Point A₄, is assumed to be at the equivalent average temperature that is the minimum

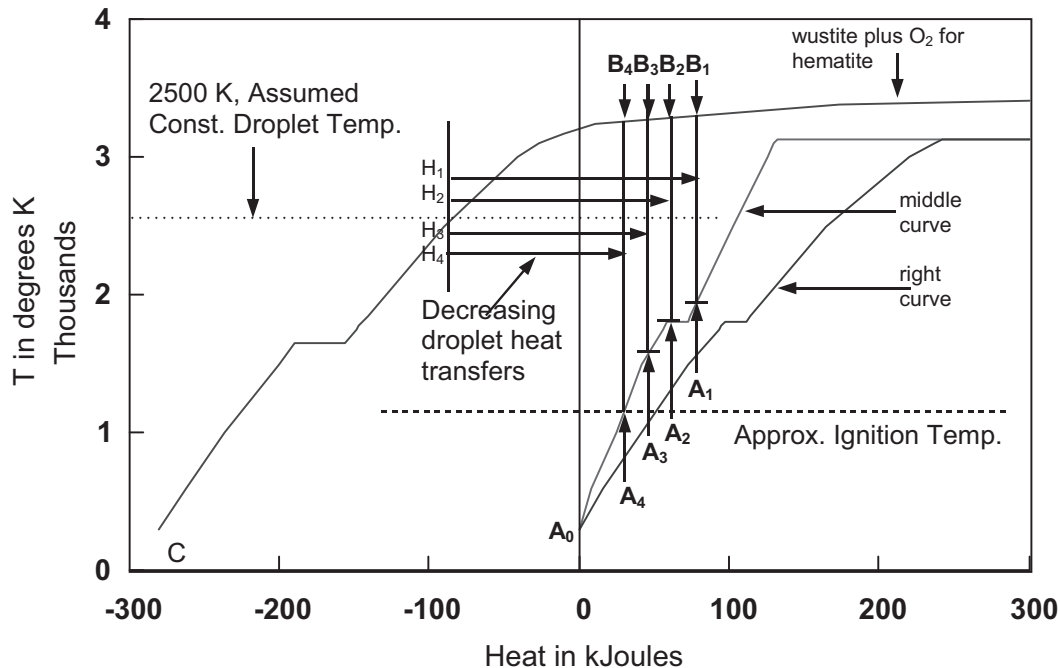


Fig. 4—Thermo-profiles for about 1 gram-mole of iron with 1.5 mole monatomic oxygen and 1 gram mole of wustite ($FeO_{1.056}$) with leftover oxygen separated by the heat of combustion .

needed to produce ignition (about 1143°C [11] but shown at a lower level on Figure 4 for clarity). If HAZ₄ at Point A₄ combusts to point B₄, and can transfer heat H₄ upon cooling to 2500 K, then its heat losses must be such that the HAZ it produces is capable of again yielding the same previous equivalent composite average preheat as was achievable at point A₄ for the previous droplet, or the combustion will cease, since any greater heat losses would not allow achievement of the minimum temperature required.

If point A₄ can be attained then every following droplet may also produce the same affect and the combustion will continue in equilibrium (equilibrium combustion as is, after all, the goal to measure in the oxygen index test).

Hence it may require numerous droplets to detach before this point can be inferred. Yes, there may be some metals for which the first droplet after ignition detachment (due to HAZ₁) will insure heat losses to exactly place the second droplet at the threshold, but the fact that many tests observe long series of droplets (long propagation lengths) before extinction prevents drawing that conclusion in general.

Disputing Basis 2: The Fall-Back

It has been argued that whether Basis 1 is wrong or not, the new criterion provides a threshold measurement that is inherently equal to or less than the true (equilibrium combustion) threshold. Therefore it is conservative and is an acceptable substitute that simply provides a greater margin of safety. *Not so.*

ASTM G 124 has always cautioned (in its paragraph 1.2) that it “provides a basis for comparing the combustion behavior of materials.” This is consistent with the usage of data from

D 2863 and G 125, the oxygen index test from which G 124 was derived. Indeed G 124 warns: “No criteria are implied for relating these data to the suitability of a material’s use in any actual system.” This latter point does not exclude [but does not provide for] the use of such data to support definition of actual operating conditions, and indeed similar data have been used to support the establishment of “exemption pressures” in CGA/EIGA piping standards. And the writer does not contradict this process.

It is, indeed, valid to use an acceptable material at a pressure lower than would be established based upon its threshold for equilibrium combustion, however, this is the *second* step of the process. One must first get to the second step. The use of “more conservative” criteria like this can invalidate the primary purpose of G 124: “comparing the combustion behavior of materials.”

In other words, one can develop exemption pressures for a series of metals that are valid but the ranking of those metals on the basis of exemption pressures can be seriously flawed.

For example consider the following syllogism for the threshold pressure, TP, of two metals A and B: for which the equilibrium combustion (EC) pressure of A is greater than B:

$$TP_{EC}(A) > TP_{EC}(B)$$

This implies metal A is better (more compatible) than metal B, and is preferred, therefore if one uses a fraction (X) of the threshold pressure as the exemption pressure (XP), they would also rank these metals:

$$XP_{EC}(A) > XP_{EC}(B),$$

However, it is also known that when the threshold pressure is based upon the 30-mm criterion that

$$TP_{EC}(A) > TP_{30mm}(A)$$

and

$$TP_{EC}(B) > TP_{30mm}(B)$$

Unfortunately, mathematically from these latter two equations one can *not* simultaneously solve them to conclude (to infer):

$$TP_{30mm}(A) > TP_{30mm}(B)$$

In other words, if $TP_{EC}(A) = 700 > TP_{EC}(B) = 500$, then metal A ranks better than metal B. Assume one allows the exemption pressure (XP) to be 80% of the threshold pressure, then we find $XP(A) = 0.8 \times 700 = 560 > XP(B) = 0.8 \times 500 = 400$ psig. And then

$$XP(A) \text{ is better than } XP(B)$$

Hence based on exemption pressure, metal A still ranks higher than metal B.

However with the 30-mm criterion, assume that a recognized and acknowledged inversion⁸ occurs and that $TP_{30mm}(A) = 400$ psig, while $TP_{30mm}(B) = 450$ psig. Then $XP(A) = 0.8 \times 400 = 320$ psig, and $XP(B) = 360$ psig. And, suddenly,

$$XP(A) < XP(B)$$

Therefore as has been admitted, now metal B ranks higher than metal A. So while the new exemption pressures are still individually valid albeit more conservative, one has lost the ability

⁸The measurement of a 30-mm threshold is inherently a crapshoot. There is scatter in the distribution of burn lengths that are measured, and in some cases the more compatible metal may not experience an early 30-mm burn at the same rate as the less compatible material and so may appear less compatible. Or inverted.

to identify the best practical metal to use. And this is a problem, especially in litigation.

A Layman's Look at Litigation.

ASTM G 88 Designing Systems for Oxygen Service contains in its Section 7.2 on Final Design a number of generalized principles including: 7.21 *Use only the most compatible of practical materials and designs.* It proffers that: "In most systems the cost of using only the most compatible materials and designs is justified by the additional safety that is achieved." This is perhaps the only generalized principle that is not founded in fire science, but rather in the influence of litigation on oxygen system design. A layman's essay on this topic follows:

Strict Liability

According to Wikipedia (See the Product Liability section therein) in the 1960s, the legal theory of strict liability evolved. This is consistent with the writer's experience. It assigned responsibility for many kinds of defects in materials and designs to producers even when there is no intent or negligence involved (on the apparent basis that only the producer can affect this aspect). The writer has often heard it described as a requirement to eliminate all known defects that can be eliminated and to warn about all known defects that can not be eliminated. This is why one can buy an electrical extension cord today with a firmly attached huge label shot full of warnings and alerts that may seem longer than the cord.

When a lawsuit boils down to strict liability issues, one can find themselves on a witness stand being asked: "Why did you use this metal, X, in this oxygen system?" And one of the better answers is to be able to honestly testify that it was the "best (most compatible) of practical materials." Most other answers allow one to then be asked; "Would more fire resistance practical material Y have worked and owing to better fire resistance prevented the incident?" If that is the case, then the witness will soon face the question; "Why did you decide to use a lesser material (to save a few dollars, to make installation easier, to make the part last longer) and condemn my client to a life time of disfigurement or whatever?"

Hence if one has not used the most compatible, practical material, one has not eliminated all known defects and is in a heightened state of vulnerability.

The practicality aspect has been recognized as crucial. It has, therefore, been recognized that it is impractical to make oxygen systems out of gold to achieve the maximum in fire-resistance. And so cost is a valid practicality issue, but where to draw the line between gold and carbon steel is where the judgment of qualified technical personnel comes into the picture.

This is why the data for promoted combustion in Tables X.1 of G 94 provides two layers. First it ranks the metals. Higher threshold ranking is better. Then after a metal is chosen as the best of practical materials, it is fine to use a lesser more conservative measure of the threshold or incipient threshold or onset threshold or other to set exemption pressures and the like.

However, the new criterion admits that it can alter the ordinal rank of metals for use in a way that is contradicted by the earlier criteria. If one needs the true threshold, then it is easier to just use it to set the exemption pressure. But if the metal choice is fixed in some way that is not dependent on the best practical metal, then the use of an incipient or onset threshold like the 30-mm criterion is acceptable.

Is There Another Way to Measure Thresholds?

Clearly historical fire limit practices are difficult to implement in testing metals. That is why for two consecutive decades efforts persisted in G-4 to simplify the positive test criterion of G 124. Is there another way?

In the writer's last two or three negative ballots, he proposed alternatives. Perhaps far-fetched alternatives but they warrant mention. The original criterion (complete combustion) was established in the early 1990s. Prior to that time, metals test data were all on small specimens and the change to actually test rods was increasing the scale of testing by orders of magnitude. It was a quantum leap better.

Assorted efforts were made to test plates and tubes, and rods. For many, the model for G 124 was the oxygen index test (D 2863) and a lot had been learned about establishing those thresholds, and those lessons were baked into G-4's own oxygen-index variation G 125. All of it is pertinent to determining thresholds by G 124, however, all of it depended upon directly watching the combustion, something easy to do in an open atmospheric-pressure test in a glass vessel with an upward flow to sweep combustion smoke away from the field of view. However, at the time, the thought of directly and closely watching the combustion of metal specimens in a high pressure stagnant-oxygen vessel was simply unrealistic.

The oxygen index used a distance or time criterion. If the specimen burned like a candle for three minutes or if 50- to 100-mm were "consumed" (and in most cases at the threshold the two criteria occurred at about the same point), then the test was considered to be above the threshold. However without direct observation, G 124 could be based only on a distance criterion. And since the equilibrium combustion threshold is the lowest condition that will just allow self-sustained combustion, the most favorable indicator of being at the threshold was the lowest condition at which the specimen combusted "completely" (adjusted for any interference by the sample mounting) for the longest practical specimen that could be accommodated. Much testing was accomplished with 3-in. long specimens but soon everyone shifted to 6-in long (150-mm) rods and for a time that was the practical limit for G 124.

In the oxygen index test, combustions that persisted for 50- to 100-mm of propagation or for 3 minutes of time, were considered positive results at or above the threshold, *but the combustion had to be in equilibrium*. Even if a specimen burned for the maximum length or for three minutes but exhibited continuously decaying (or accelerating) combustion (and some materials did before extinction) then it was a potential basis for scoring the result as a negative. Therefore in principle a complete six-inch burn in a test by G 124 was the most probable result to score as a positive, even though the equilibrium of the combustion could not be verified, which was another factor in adopting the extra length.

Direct observation was not considered realistic. Windows large enough to expose the full specimen were costly and massive. And if even if one had such windows, there are metals, like aluminum that produce too much dust in a stagnant atmosphere to allow visibility.

Since then other ways to "observe" combustion have been tried. Windows have been designed and used that can allow line of sight. Infrared or x-ray cameras have seen through the dust clouds of vapor-burning metals. Gravimetric testing has measured the dynamic weight of the specimens. Ultrasonic length measurement has inferred the velocity of propagation (though the effects of ultrasound on the combustion at the threshold would have to be established).

If any of these methods can be validated to infer equilibrium of the combustion, then the

need for a long successful burn to establish an equilibrium combustion threshold would be eliminated. Alternatively, the current standard can be disclaimed for its current primary purpose, or cloned into a second “onset” or “incipient” standard to rank metals, and instead be used only for setting use (exemption) pressures for metals that have already been validated on other bases. However, the ranking inversions that have been stipulated, are a potent contradiction of the use of a 30-mm criterion (or other short criterion) for the primary ordinal purpose.

Summary

The positive-burn criterion for ASTM G 124 was changed in 2010 from complete combustion of a long specimen to any propagation length of 30-mm or more. The change has been disputed on the basis that the new criterion renders the standard unfit for use for its original and most important purpose to rank metals compatibility. This analysis has alleged that some metals may require much more than 30-mm of propagation to coast into an equilibrium combustion mode that is vital for these data to rank a metals compatibility. However, the shorter criteria appear valid for setting exemption pressures of metals known to be compatible or that are mandated for use for other reasons. Alternative ways to assess equilibrium combustion were cited that might reduce the amount of testing to establish an equilibrium combustion threshold, but which might require more complex and expensive equipment.

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Barry L. Werley¹

ASTM Standard G 124 (2010, 2018 Versions) Is Unfit for Use

REFERENCE: Werley, B. L., “ASTM Standard G 124 (2010, 2018 Versions) is Unfit for Use”, Self-published opinion, *The Saga of ASTM G 124; How a Standard Intended to Make Oxygen Systems Safe Became Unfit for Use*, Public service opinion, Public Domain 2020, 48 pages.

ABSTRACT: A revision of the positive-burn criterion of ASTM G 124 in 2010 marked a change apparently viewed by many as an obvious much-needed long-overdue evolution but was viewed by the writer as a revolutionary, unjustified change that renders the standard unfit for use, and is potentially difficult to defend in litigation. History and prior justifications for this conclusion and its remediation are elaborated upon and extensively expanded .

KEY WORDS: criterion, promoted combustion, ignition, self-sustained combustion, fitness, strict liability.

Introduction

This analysis/opinion is an elaboration (2019) of an earlier elaboration (2014[1]) of a still earlier elaboration (2010 [2]) of an even much earlier analysis (2002 [3]) based on numerous negative ballots the writer has issued dating to the early 1990s regarding a single controversial issue unpinning ASTM Standard G 124 on “*Determining the Combustion Behavior of Metallic Materials in Oxygen-Enriched Atmospheres*” [4]. As such it will recapitulate many of the points in these earlier arguments, but will present new materials and analysis to still further strengthen the case.

The writer is a retired Hazards Research Specialist who worked for more than 27 years, testing and evaluating the fire and explosion properties of materials. He is also a charter member (1975) of ASTM Committee G4 on Compatibility and Sensitivity of Materials in Oxygen-Enriched Atmospheres, a past chair and has held most offices at one time or another, and received their second Award of Merit in 1989 and is therefore a Fellow in the Society. In that capacity, he was present and active, and played a significant and claims a major role, in the development of ASTM G124, an effort that began in the 1980s. This latest elaboration is intended to further illustrate why the change made to this standard's procedure in 2010 has rendered it unfit for its primary purpose.

In any attempt to determine the cause of a fire incident involving an oxidant, an aggrieved individual or company or plaintiff might wish to consider whether “the most compatible of materials and designs” were used or whether data from G 124 might have led to the

¹ Retired, archive paper, no address.

² Italic numbers in brackets refer to the reference list at the end of the paper.

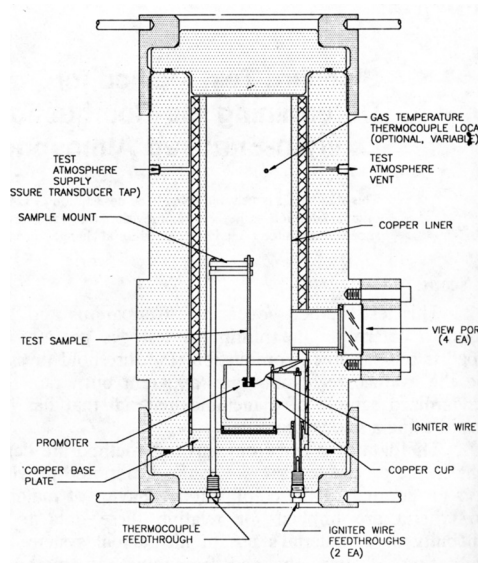


Fig 1—Typical Stainless Steel Test Chamber Cross-Section from G 124.

use of less than the most compatible of materials. Since most of the history of how standards developed is obscure or unwritten despite being public information, this analysis is offered to address the specific issues with G 124.

G 124 published in 1994 and measures the fire limits of metals. Its primary purpose is to *rank* metals. If one metal has a higher fire limit than another, then in the absence of any compelling ancillary issues, like practicality, the first metal is considered the more compatible, therefore preferable, for use in oxygen hardware to minimize the risk and consequences of ignition, fire and explosion. In recent years (actually about ten or twenty), data measured with G 124 have also been factored in to set actual operating conditions for some applications, but this analysis does not address nor challenge that use.

The G 124 test involves placing a series of metal specimens into an oxygen or other oxidant atmosphere in a vessel such as the typical example shown in the standard (Figure 1) and igniting them. One seeks to determine the threshold condition *above* which the metal will just "burn by itself" in the test configuration, meaning will experience "self-sustaining" combustion that meets or exceeds equilibrium-combustion conditions as are described in some quarters, ...wherein it may burn extensively or even completely. Thereby one can also determine by inference, the threshold *below* which it will not burn *by itself*, will **not** experience self-sustaining combustion even though it may experience a transient or what is also called "flame-cap" combustion, and what will be referred to here, at times, as "ignition-sustained combustion". The former combustion can yield large and destructive incidents, the latter is more likely to yield limited, perhaps very limited, destruction. If a specimen of appreciable size burns completely in the G 124 test (meaning six inches for the most commonly tested specimen length) in even just one valid test, it is a strong indicator, nay proof positive, it was above its fire limit. If it burns just a little, it most likely suggests it was adequately ig-

nited but was below its fire limit. If it does not burn at all, it tells you very little.

Oxygen systems have often experienced combustion that was not sustained. It was either flame-cap combustion or sustainable combustion that failed for any of a number of reasons. In some cases plants have operated before, during, and even after an ignition event even though the event produced significant damage, and the plant just kept running, and the damage was only discovered during shut downs for routine preventive maintenance.

However, in some other cases, combustion has been self-sustained. Sustained to the point where damage was so great the whole system or plant and even peripheral locality was lost and in some cases multiple fatalities have resulted.

G 124 was intended to focus most on prevention of the latter kind. This is not to say that the former cases can not be important. Indeed, a standard to measure flame-cap limits might have real merit, though the G 124 procedure might not be the best approach to do that, but clearly catastrophic events, which thankfully tend to happen less frequently, were the more important to control.

When one uses a practical metal ranked highest by this test, one is intending to build the most compatible of the possible practical systems as has been, and is, encouraged by ASTM Standard G 88, "*Designing Systems for Oxygen Service*" [5], which beginning in the 2005 version recommends in its section 7.21 "Use Only the Most Compatible of Practical Materials and Designs."

If one uses a lower ranked metal... or if G 124 does not correctly rank the metals,... then the resulting system will not be the "most compatible" and it will present a greater risk to all three of Committee G-4's key missions namely to avoid damage to: (1) People, (2) Systems, and/or (3) System Missions.

Sometimes, however, specimens will clearly burn much more than a little but yet will self-extinguish far before burning the entire specimen. The bone of contention here regards how to score results like these; Are these above or below the fire limit?

From ~1994 to 2010, sixteen years, a positive burn was defined as combustion to where the specimen holder might interfere with further combustion, and any such intermediate results were conservatively scored as being below the limit. However, after the 2010 revision (which the writer strenuously opposed and continues to oppose), some are now scored as being above the limit if they burn further than a new distance criterion added to the standard then and called the "the burn length criterion" (BLC). This "burn criterion" was set at about 1.18-inches (30-mm) of combustion above the igniter as shown on Fig. 2.

The desire to use a short burn-length-criterion did not emerge in 2010. It was not a new idea. In the very first ballot of G 124, Circa 1992, a short criterion was proposed by a cadre (one is tempted to refer to them as a clique) of key members, sort of like a cogno-scente. The writer cast a detailed negative ballot presenting the case for why such short burn lengths do not reflect self-sustaining combustion, and the argument was found persuasive by that earlier generation of G-4's members, and the standard adopted complete (meaning about

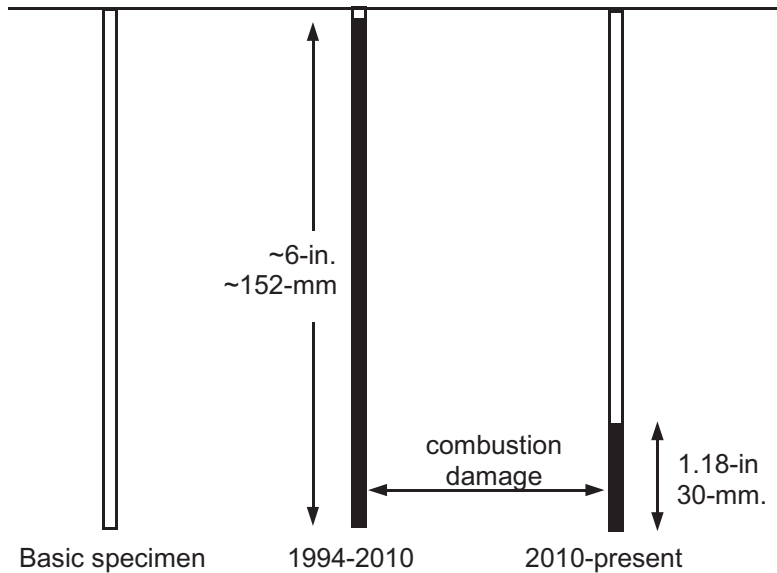


Fig 2—*Burn Length Criterion as defined in 2010.*

six-inch) burn lengths to reflect positive results.

However, that cadre or clique of short-burn devotees was clearly not convinced nor daunted. However curiously, there was no effort exerted to make a technical argument nor publicize a reasoning for the short criterion they wanted so much. Between 1992 and 2010, the short criterion was simply repeatedly balloted, with no defense, and each time, the writer re-cast negatives in much technical detail. However, while efforts often addressed, other negatives cast throughout the period, the short-burn devotees used an ASTM option to withdraw *every* ballot and simply ignore, to in effect nullify, to censor, these negatives.

In 2002, one of these ballots was issued and to spare future repeated onus, several bases were collected into a report [3] that could be referenced in future negative votes and it was made available to G4 and on the Internet.

Throughout the period (1992-2009) virtually no technical case was made for a short criterion. It was apparently intuitively obvious to the cognoscente. In 2009, Sparks et al [6] presented a "peer-reviewed" paper at a G4 Symposium in Berlin the year before. It concludes the prestigious NASA White Sands Test Facility (WSTF) has measured the maximum burn length beyond which igniter influence is dissipated and therefore self-sustaining combustion is consequentially manifest, and declares that "all metals that burn a distance greater than 30-mm (1.18-in) are burning independently of any promoter effects that pre-heated the test sample during the ignition process." This was based on an average measured test result plus three sigma and a 50% safety factor.

As the principal and perhaps last antagonist to this thesis from the earlier G-4 generation, the authors might have requested the writer to comment. They did not. Perhaps the new criterion was just too obvious. The editors of the STP into which it was published, (which included members of the short-burn devotee cadre/clique and one or more co-authors

“...The reason for the revision is the-5 year review/ release. While doing this review the committee chose to include some long overdue changes based on the current level of understanding of the state of the art in metals combustion testing.”

Fig 3—*Rationale statement for 2009 ballot.*

“The Committee is not aware of any published research showing igniter chemistry above 30mm.” and

”Committee is unsure of a method to compare the two standards G124 and G125 (Oxygen index).”

Fig 4—*Bases for non-persuasive vote, 2009.*

of the actual paper [6]) might have asked the writer to be one of the peer reviewers or for informal comment. They did not.

A ballot soon launched with what the writer considers to have been a misleading rationale for the G4 Committee at large, Fig. 3, with what seems like a statement of obviousness, calling the revision merely "some long overdue changes based on the current level of understanding of the state of the art in metals combustion testing". To the short burn devotees, this change was apparently trivial, as well as obvious.

During Committee review of yet another negative from the writer, a copy of the "definitive" Sparks et al paper [6] was emailed to the writer who was asked to therefore withdraw his negative. Overnight at least two flaws in the paper were identified, and later still more would be found. One flaw was an assumption that all igniter materials drain from a burning specimen when the first droplet of liquid slag falls and this analysis will build upon earlier discussion of that issue in more detail later.

As a result the negative was found non-persuasive with not one word disputing its many analyses, Fig. 4, but rather because no one at the meeting was aware of any publication of the data cited, which had not in fact been published. Furthermore ignorance was professed of how to use another of G-4's standards, G 125 [7] that addresses similar testing and interpretation. The NASA-WSTF results, were then cited as if Gospel, and the negative was found consequently non-persuasive. Not on its merits but in support of the cognoscente.

The writer considered this 2010 change not only ill-advised but dangerous. In his opinion, his judgment, it will and may already have resulted in deployment of systems, consistent with the newer ASTM standard, that are not only *not* the most compatible of practical options, but which may have already done harm and caused injury or death. And the manifold technical bases for this negative had been ignored at that time, for more than 18 years, and for more more than eight additional years since then.

“...During the April meeting, the committee discussed and brainstormed possible shortcomings and areas for improvement in the standard; however, no input was given by the subcommittee members that the standard is dangerously flawed and should not be approved. This along with the fact that there were no additional negative votes indicates a common understanding that the standard is applicable and useful within its scope. ”

Fig 5—*Basis for non-persuasive vote, 2017.*

The following year, 2010, the writer’s concerns were elaborated again [2] again to no effect.

Still later, on the basis of the small number of voters in both the subcommittee and main committee votes used to over-ride the 2009 negative, an appeal to the ASTM Committee on Technical Committee Operations (COTCO), resulted in COTCO advising that G-4 could define a consensus with as many or as few votes as it wished.

In 2014, another elaboration [1] of the claimed issues with G 124 was prepared and distributed.

When G 124 came up for mandatory review again in 2017 and was balloted for re-approval. The writer again voted negative. A few cosmetic unrelated changes were made *just to get them out of the way*. But that had the effect of re-approving the faulty criterion for up to another eight years. Another negative was cast citing that tactic as a finesse that re-approves the standard without addressing a major flaw. It seemed a bit like when one political party agrees to lower taxes later in exchange for increasing them now, and the increase happens but the decrease never does.

A full committee ballot to find the second negative non-persuasive, Fig. 5, was based upon, (1) no one at the prior meeting (which the writer did not attend), spoke out about any dangers of G 124, and, (2) the fact that there was only *one* negative vote proving there is "a common understanding that the standard is applicable and useful within its scope."

And so this bone of contention persists as to whether using the altered 2010 criterion can result in erroneous metal rankings. And the writer’s contention has been and continues to be that it can and will.

ASTM Committee G4 is comprised to large extent by those who, build, operate, and design oxygen production systems, and are liable for their performance, and has few if any small volume end-users, who also can be by-and-large the victims of incidents. This bone of contention here boils done to whether G 124 can support, as contended here, the design of inadequate systems. So this elaboration was given as brash a title as possible to explain, defend and justify all of the past negative votes.... all of them because of this same one bone of contention...the burn length criterion that should be used to define a positive burn. Perhaps

there will never be another oxygen incident. But, if or when incidents in oxygen occur, any individuals or companies that may fall victim, if this thesis is correct, can understand why this aspect, if it proves valid, may have been a causal factor.

Since ASTM has no mechanism requiring acknowledgement or warning of dissent to the consensus in its standards nor even to cite how big or small the "full consensus is" that approves them, and since its procedures allow for censorship of dissent, and since communication between a rather cloistered leadership and G-4 at large is not only spotty but appears at times to be deliberately or at least conveniently obscure, this issue can be inadvertently and/or deliberately "influenced", when it appears that for so many years so many experts have apparently relied upon intuitive obviousness rather than historical precedent and laboratory study to support their conviction,

This rather unbecoming approach of apparently ignoring dissent in favor of intuition reflects badly on the integrity of G-4 and ASTM, and implies the writer is a commentator of no credibility nor qualification. Hence this elaboration of past arguments, correct or not, will defend the writer's experience and training in this area, before addressing the primary and fall-back positions of the Committee and before trying to resolve some of the test's onus.

Voir Dire

Definition: "A preliminary examination of the competency of a witness or juror"

This voir dire is presented because of the frequent and summary way negative ballots on this issue have been ignored and in some cases belittled. Clearly, on the one hand, this writer's credentials in this area are suspect in some quarters. However, on the other hand, the described bone of contention, may be just so intuitively obvious (even though arguably wrong), it may be too hard for too many key players in ASTM Committee G-4 to wrap their minds around any other perspective even if it is from a source they respect. It could be like the paradox of whether the earth is flat or round. Any fool can look outside and see proof that the earth is obviously flat. So this section will try to defend the writer's credibility and specific experience to even dare to challenge the "new" G 124.

The writer's first involvement with fire-limit testing and its application to metals, nonmetals, and gases, began in 1966 when he was a minor figure supporting Dr. Abraham Lapin (the G-4 Committee's primary patriarch) in the defense of a lawsuit in which (1) the oxygen concentration at which steel will burn and (2) the rate at which oxygen from liquid pools can enrich an environment were both factors. He collected the ambient enrichment data that Dr. Lapin published several years later.

Fast forward to 1972, when he re-joined the oxygen compatibility efforts and at that time metal flammability was a rapidly growing concern that would occupy an appreciable fraction of his efforts.

In the mid-1970s he was fortunate to attend what was one of the first if not the very

first offerings of Dr. Chester Grelecki's AICHE Course "*Fundamentals of Fire and Explosion Hazards*". Dr. Grelecki was very active in the early formation of ASTM E-27 on *Hazard Potential of Chemicals* that addresses gaseous fire-limit hazards, and over the years, the fire limit practices covered in that course proved a vital resource. He was fortunate to work with Dr. Grelecki's Hazards Research Corp, numerous times in the 70s and 80s on fire-limit and explosive studies.

He always made it a key point to distinguish between flame cap and self-sustaining combustion fire hazards in frequent fire-hazard introduction topics for new research department hires and for fire-hazard refresher training.

In one instance faced in the 70s, there was a need to know if one especially toxic gas had a low lean-fire-limit. It had a 0.05 ppm TLV and in those days, and apparently today yet, TLVs did not come any lower. Although gas-phase fire limits are commonly measured in a fairly large diameter (several inches) glass tube with a long length 3-4 feet, that quantity of this toxic gas was more risk than he wanted in the lab, and even in the building. So he pitched measuring a flame-cap limit to Dr. Clyde McKinley, his research director, (who was another important G-4 patriarch), and then proceeded to scale down a test vessel volume by a factor of about 100. It was known this would only measure a flame-cap threshold below the true fire limit minimum. Luckily, these flame-cap limits were found at a concentration not greatly below what theory would have predicted for the true limit. It helped remedy a spill of the gas. So this indicates the writer is not unaware of nor opposed to using flame-cap limits as conservative approximations...when reasonable.

Among other fire-limit issues encountered in those 1970s was that tragically the first edition of the ASTM D 2863 "*Measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion of Plastics (Oxygen Index)*" standard [8], from Committee D-20, the standard upon which G 124 later evolved (as a pressurized oxygen index test), was poorly written. This is important because D 2863 is the foundation upon which G 124 was built.

D 2863 had been adopted by Drs. McKinley and Lapin as one of three tests to evaluate materials for oxygen service. Dr. Lapin had published a seminal paper titled "**Oxygen Compatibility of Materials**" [9] that studied how to weight the three tests results. These results were a factor in Dr. Lapin's later push for the G-4 Committee to be formed.

D 2863, the oxygen Index test, was clearly written to be a fire-limit standard, but its language was vague and its procedure actually specified measuring the circumstances at which a specific combustion velocity resulted. If a 70-150 mm (3-6 inch) specimen burned like a candle for more than three minutes or to a length greater than 50 mm then the oxygen concentration was to be decreased for the next test. If it burned for less than three minutes in less than 50 mm, then the oxygen concentration was to be increased. Hence, for years testing had sought to measure where specimens would burn exactly 50 mm in exactly 3 minutes. Often interpolations were used.

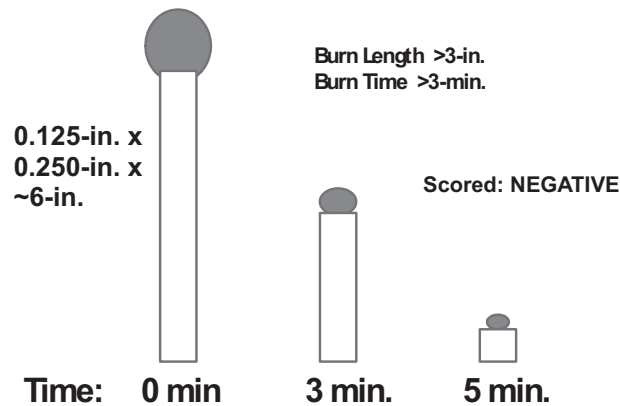


Fig 6—Curious example of filled PTFE rod test.

The writer wrote to the D-20 chair seeking clarification, and the second edition corrected the language. This led to an assignment for him to go through years of previous data, throw away a lot of expensive testing for those materials that could not be resolved into a true fire limit,...to indicate where the data only supported bracketing a limit,... To launch further testing where the original materials were still available and sufficient or could still be obtained,and after that to often join in evaluating specific curious test results, like some that will be reviewed here shortly, as to whether they did indeed define self-sustaining combustion as intended by D 2863.

Much of the wisdom garnered back then was incorporated by the writer years later into G-4's own spin-off of the Oxygen Index standard G 125 “*Measuring Liquid and Solid Material Fire Limits in Gaseous Oxidants*” [7], Section 12. All of them related to time-tested methods of inferring self-sustaining (equilibrium combustion versus transient ignition-induced flame-cap combustion. Two examples are worth noting:

(1) *Nonequilibrium Combustion of Filled PTFE*. For example, the OI test calls for that 3 minute burn time or 50 mm burn length to be a positive result (meaning at or above the fire limit). In one situation where a fluorinated polymer, probably a filled PTFE was ignited with a robust flame (Fig. 6) perhaps the size of a dime on its top 1/8 x 1/4-inch surface.

It could be watched as it took about five minutes to extinguish and it burned over 100-mm. But during those five minutes, the flame continuously shrank. And at the last instant before extinction it was only perhaps an eighth of an inch in diameter. Even though both the time *and* distance criteria were met far more than the criteria specifies, *it was scored as a negative result*, and a

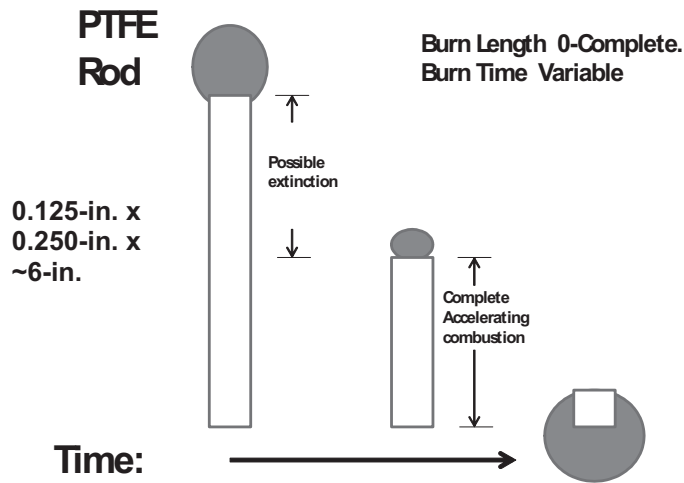


Fig 7—Curious example of a critical burn length.

later section will explain why.

(2) *Critical burn length.* For another curious example, Fig. 7 exhibits what will be called a "critical" burn length here so it can be referred back to later when some important NASA data are dissected. A curious behavior was observed when burning long PTFE rods. They could be ignited on the top, and watched as they burned downward with a shrinking flame size like that just described above. Sometimes they would go out. But sometimes, they would reach a "critical" point that turned out to be related to the specimen position in the vessel, at which time the shape and intensity of the shrinking combustion would change itself and accelerate until the entire specimen was consumed *every time* with a growing robust flame. The flame might go out before it got to the critical point, *but if it got there, then it burned to completion.* Something similar to that may be affecting metals tests that will be examined later.

Fig 8, depicts how the apparatus suffered from eddy currents that formed at a specific location resulting in the surface velocity of the oxygen along the upper half of the specimen being upwards, carrying heat of combustion away as was expected, and making combustion more difficult, but that below the critical level, the surface flow velocity flipped and was downward, even though it was in an average upwards flowing stream, producing a much more flammable and accelerating-combustion scenario.

Any specimen that burned down to this critical point in the vessel was almost assured of complete combustion, but above this point the burn lengths were variable and scattered. If the specimens were mounted a little high then the result would be incomplete combustion. If they were mounted a little low, then complete combustion was almost always the result. This

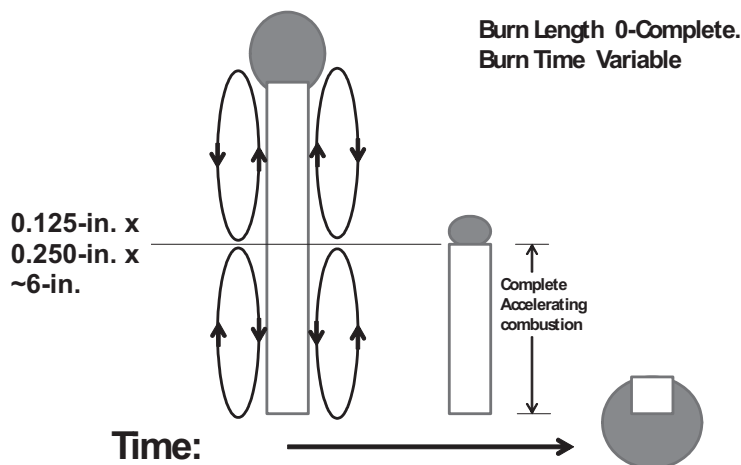


Fig 8—Prior curious examples explained.

experience will also be cited later on when the writer speculates on some similar NASA test data.

The oxygen index test was originally intended as a QC test for plastics, and so the standard's guidance was being exceeded when liquids were tested, and metals and other materials, and pressure and temperature as well as oxidant concentration were varied and sometimes the chemistry of the oxidant itself was changed, but the principles learned could then be extended to other tests.

In the late 1970s, Dr. Michael Benning, who chaired G-4's second symposium producing STP 910, and the writer published a paper [10] in it on the threshold of combustion of carbon steel in terms of oxygen concentration and pressure, and also briefly studied temperature effects.

In the very early 1980s, Dr. Benning, designed a statistical experiment and published a second paper in *STP 910* [11] on the thresholds of polymer combustion at elevated pressures. The writer designed an apparatus and supervised its building and the testing of six polymer materials in support. Dr. Benning developed an analysis of their behavior that would become critical later when testing of metals was undertaken.

Those results led to the writer redesigning the apparatus for metals testing. In the early to mid-1980s John Zabrenski came on board and began testing a wide range of metal rods for their fire limits, in that apparatus and other equipment of his (Zabrenski's) own design and in *STP 1197*, Benning, Zabrenski and Ngoc Le [12] reported on the Flammability of Aluminum, and their discovery of the crucial importance of trace inert gases in oxygen and the basis for that importance.

Our consultant Prof/Doctor Irvin Glassman (Keynote Address speaker in ASTM *STP 1111*) played Devil's Advocate for the project attempting to disprove the results and

Benning's analysis. Ultimately, Dr. Benning's original analysis was proven correct, and Dr. Glassman modified Chapter Nine in his 1987 Second Edition of his standard text "*Combustion*" [13] titled "**The Combustion of Nonvolatile Fuels**". Previously it had addressed only the combustion of carbon char, but after that addressed metals combustion as well.

Zabrenski's aluminum data also led to a company and personal campaign of the writer to urge anyone who tests fire limits to analyze and report the actual analysis of the actual test gases used. As with the G 124 burn criterion issue, less than 100% success was achieved in this area also.

To this day one can still see papers published that simply report use of commercial grade oxygen (about 99.6%+) or Aviator's Breathing-Grade oxygen (about 99.5%+). Yet, depending upon the precise composition of these "oxygens" above these minimum standards, they can result in certain metals being either non flammable, or capable of flame-cap (transient limited range) results, or can produce devastating high-speed combustion that can be as destructive as some high explosives.

And commercial gas purities varied widely within this range, throughout the industry and in general the average industrial product purity was rising, as was the average risk of fire. Systems incapable of combustion in the oxygen of the 1960s might be highly combustible in some of the oxygen available today.

This subtle fire-limit fact has proven so counterintuitive as to be insidious. When Professor/Doctor Kenneth Kuo (author of the standard text: "*Principles of Combustion*" [14] began testing aluminum in oxygen in support of several CGA pamphlets in the 1990s, he began obtaining rather bland results with Brand X "commercial grade" oxygen and was stunned when he was sent zero-grade product (99.9%+). Perhaps this aspect is so counterintuitive that one can only really appreciate its significance by personally testing the two purities of "Oxygen" and witnessing the Jekyll-to-Hyde transition that occurs between non-flammability, flame-cap and true self-sustaining combustion above the true fire limit. Maybe one has to touch the hot stove to learn not to touch the hot stove.

Dr. Glassman's previously cited textbook [13] was an important resource in the writer's negative ballots also. In at least three editions [13,15,16] of it, Dr Glassman discusses fire limit tests in Chapter 4, and comments that in a gas-phase fire-limit testing vessel, a "4-ft length is chosen in order to allow an observer to truly judge whether the flame will propagate indefinitely or not." Erratic extinguishment and flame caps, have always presented this same kind of dilemma in gas-phase testing that they present in testing under G 124.

John Zabrenski's later testing of metals other than aluminum led to many other significant observations. He began testing 3-inch long specimens in 0.125- and 0.25-inch diameters, and as the writer recalls he had difficulty determining the thresholds with 3-in long specimens and changed to 6-inch. Zabrenski sought complete combustion results per the previous discussion but evaluated every result individually to see if exceptional behavior was

present. Ultimately on the basis of numerous tests, probably hundreds, he concluded that the fire limit for 0.25-inch diameter 304 alloy stainless steel rod was 725 psig. These results were published by Zabrenski, Slusser and the writer [17] in 1989.

Dr. James Hansel and the writer [18] would later report on follow up with still more testing of similar stainless steels, about 200 more tests, without contradicting Zabrenski's results using his same approach.

Back then, in the 1980s, the writer had become smitten with a bold idea. *Perhaps one did not have to use a complete combustion result to demarcate the limit.* Zabrenski had often seen small scale propagations below his ultimately determined threshold and he had often seen results that propagated significant distances before extinction. They were always a quandary. Perhaps one did not need a full combustion to define the limit? It seemed so obvious but the writer knew of no definitive data. However, the writer did know that that is *not* how gas fire limits are measured. And that gave him pause. Such a result could also invalidate much of Zabrenski's testing.

Zabrenski changed assignments in the mid-1980s but owing to his own reported numerous issues with stainless steels, he left the lab with a slew of 304 rods from the same batch he had tested so extensively before declaring a 725 psig threshold. The writer set out to see whether there was a chance that 304 rods tested below Zabrenski's established threshold could ever yield long, or even complete propagations, if tested in large enough numbers, ... numbers that would support the use of less than complete combustion as a positive burn.

The writer strong-ignited six-inch long specimens in pressures somewhat below Zabrenski's declared threshold. And he found that while the vast majority of them did not propagate much beyond the area covered by the igniter, there were a few, perhaps only a few percent that did curiously burn further, indeed, it is his potentially flawed recollection they burned close to if not further than the burn criterion adopted more than two decades later for G 124 in 2010. *None burned completely.* Later, NASA data which are now available would reaffirm this result, and they shall be examined in a later section.

In retirement, the writer does not have access to these data he collected, and they may not exist anymore or maybe they will surface, but he would like to guess that he saw significantly more than the burn criterion propagation in one or two tests in that long series, but that memory may be seriously flawed or worse. So he will substitute those similar NASA data published 20 years later to make this point again in the following sections.

Nonetheless, in the early 1990s when the first ballot of G 124 was issued and it proposed using a short burn to identify the threshold. he cast his first negative ballot because of these results and helped clarify the standards wordings for the definition 3.1.4 for self-sustained combustion (meaning, complete to where the support may interfere with combustion), and the similar elaboration in its Note 7.

His data were not confidential and were discussed openly and were almost certainly cited in that earliest negative ballot. Apologies are offered that they were not published for-

mally, but frankly, in the mid-90s ASTM and Committee G-4 became a rather unpleasant place for the writer in which to publish papers. And at the time, these results were just not that important. G 124 was using a time-honored criterion and would continue until 2010.

In the late 1980s, testing of structured packing for air-separation-plant distillation columns led Dr. Brian Dunbobbin, Dr. James Hansel and the writer to provide a paper for *STP 1111* [17]. These tests revealed a very explosive combustion mode for aluminum structured packing, again based on purity of the oxygen, and led to cooperatively sponsored industry testing (the first of which was led by Dr. Kenneth Kuo, as previously cited). These data back then led to the production of Compressed Gas Association Pamphlets G-4.8 *Safe Use of Aluminum-Structured Packing for Oxygen Distillation Columns* and G-4.9 *Safe Use of Brazed Aluminum Heat Exchangers for Producing Pressurized Oxygen*.

Dr. Sheldon Dean took great interest in these structured packing tests especially with regard to the flammability of brass, and was cited in the paper for his counsel and contribution. Dr. Dean did not seek to publish his opinion.

Dr. Dean had examined several brass specimens that were bottom ignited but did not burn all the way to the top nor all the way out of the packing structure. He speculated that the droplets of slag frozen in the structure might contain portions of the igniter chemistry either transported up the specimen perhaps as far as 4 inches by surface tension or deposited on the upper regions as debris or condensate that re-entered into the slag as the droplets burned upward. He sought XRDF testing, that would have been supervised by Joseph Slusser. Unfortunately, Slusser does not recall this particular specimen among all those he oversaw. Dr. Dean reported that he did, indeed, find igniter materials. Once again at that time these were very interesting, but not particularly important results.

In 1996 Joseph Slusser and the writer sought to capture some recently theorized massive excess oxygen in a series of cryogenic quench tests of burning steel slag droplets. For several weeks Slusser participated in this effort, reporting XRDF analysis of the results, but was then deflected to other more pressing work. The writer ultimately prepared a paper "**A Brief Study of Carbon Steel Combustion Using Cryogenically Quenched Specimens**" submitted for ASTM *STP 1319*.

Unfortunately this paper stepped on some very sensitive toes and both it and a subsequent unrelated paper were strenuously rejected for publication and ravaged to such an extent in the peer-review process and elsewhere that rather than fight an unseemly and mutually destructive hostility the writer withdrew it from *STP 1319* and concentrated on successfully defending the later, more important, paper. The unpleasantness of the experience ultimately discouraged the writer and a number of coworkers, from submitting further.

Following a cooling off period of several years, the paper was self-published [20] and was openly available for numerous years. It is probably still around and it included the photograph in Fig. 9 of burning steel wire. Notice that the slag droplets that hang from these rods appears to become inflated periodically such as indicated in the lower row. Inflation is

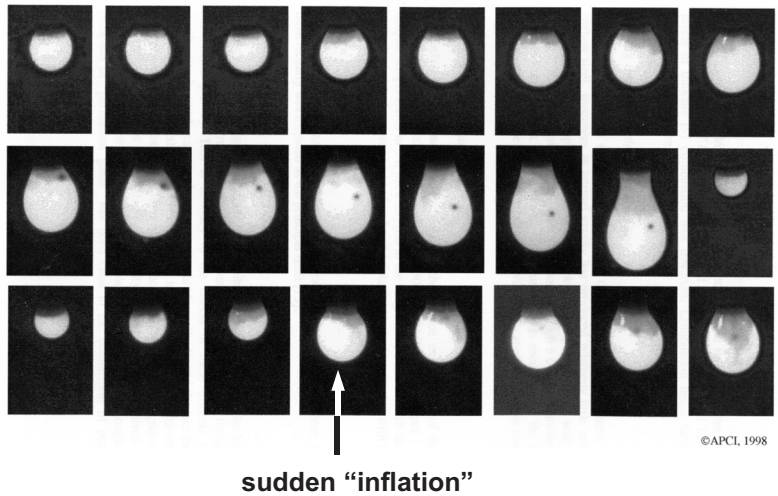


Fig 9—Droplet photos 1 [20].

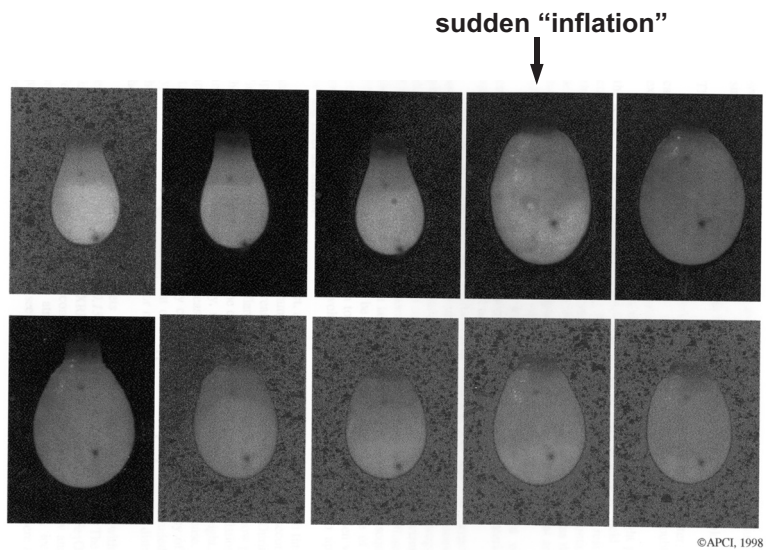


Fig 10—Droplet photos 2 [20]

especially obvious during the extinction shown in Fig. 10. The photos of Fig 11 from the report provide additional support for the notion. Dispute of this “inflation” was severe.

Molten steel in a droplet's interior appears as though it can melt and drip through an a gas annulus and attached outer igniter/slag balloon, perhaps taking some of the slag with it but potentially leaving a significant portion of the slag and its initial charge of igniter materials behind. This provides a very plausible mechanism for igniter materials to be transported upward for some distance even as successive droplets may reduce their fraction in the slag in a continuous-dilution scenario.

Notice the right-hand photo of Figure 11 shows vestiges of a gas annulus that might

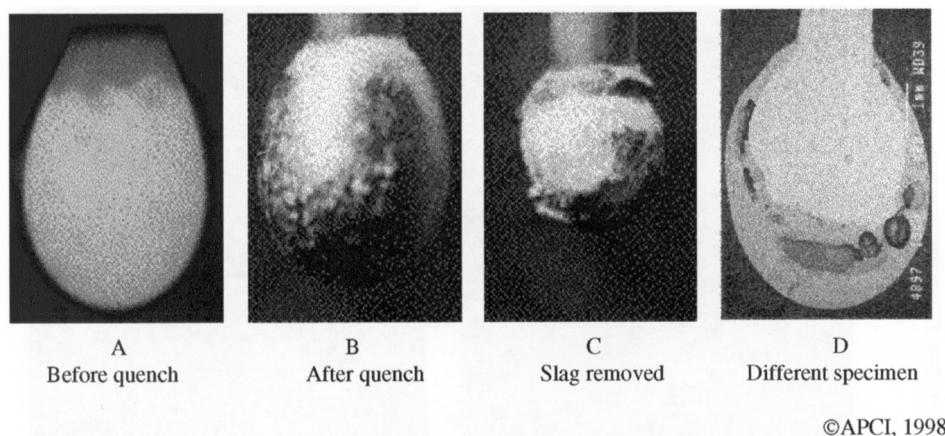


Fig 11—Droplet photos 3 [20].

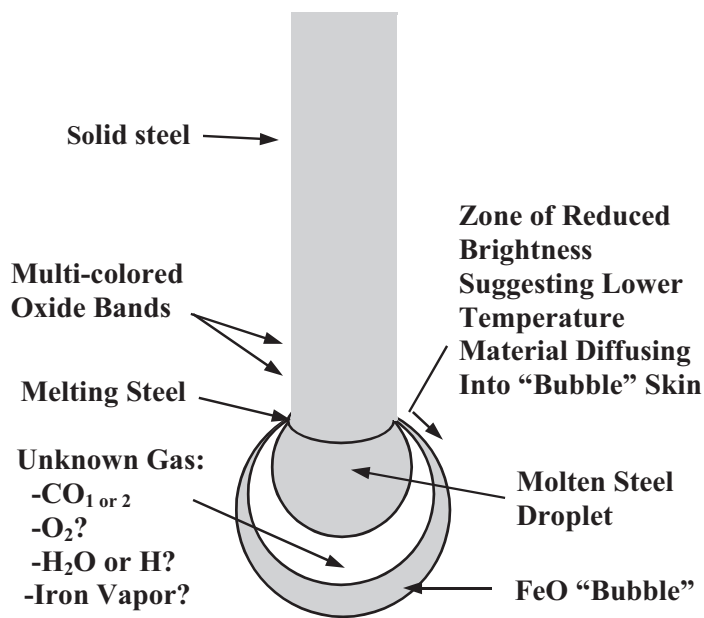


Fig 12—Potential droplet structure redrawn from [20].

have been much larger at molten steel temperatures. The Figure 12 provided writer's surmise of the slag structure.

Dr. Michael Lanyi and Dr. Zbigniew Zurecki explained this actually well-documented and well-understood behavior to the writer and Dr. Lanyi attended an ASTM Committee G-4 meeting in 1999 and presented a paper in the seminar session, and his paper appears in STP 1395 [21].

In other unreported experimentation, the writer has tested large scale specimens of tubing and pipes. These were of dimension that dwarf many of the available laboratory results being up to 4 or 5 inches in diameter and several feet long. None of these were published nor discussed publicly at that time .

This experience base, this *voir dire*, appraise it as you will, is substantial and supports the writer's knowledge base, his right to oppose the revision, and defends the original "complete" combustion criterion (as it applied at the time to up to six-inch specimens) in G 124 from 1992 though 2010, and it do *not* support a short criterion. On frequent occasions in perhaps as many as five to ten ballots the short criteria approach was nonetheless re-balloted, and this is why each time the writer provided extensive bases against its adoption in negative votes to ballots that were always cancelled and ignored. With no apparent bases, a cadre of short criterion advocates continued to press for its adoption.

The writer on the basis of his knowledge base, can only speculate that they are as smitten today, as he once was with the "intuitively obvious" allure of a short criterion. Recall again the old controversy over whether the earth is round or flat. Again, any fool can look out a window and see that its flat. However, in 2009, an experimental program and a paper from within the short criterion devotee ranks finally alleged to have proven that a short criterion was valid, and that it was a burn length equal to or greater than 30 mm of rod which they assert is clearly combustion beyond the influence of the igniter event....therefore self-sustained, such that the writer's arguments and knowledge base should not even be considered.. The reasons why this is *not* the case will be covered, again but in more detail, in the next section of this paper.

However, the writer's experience and training base overviewed here made (and makes) it impossible for him to endorse a short criterion. This background is not trivial nor irrelevant and may equal or exceed many of those holding the opposition view. And if, as suspected, apparent intuition from too-confident egos is the basis for ignoring so many of the writer's negative ballots without addressing them, then one can see how an invalid test program could have easily been designed. And yet that program, which the writer declares to be invalid, was the formal basis for finding the 2009 negative ballot summarily unpersuasive with what was virtually no cited examination of it. But can intuition and this one test program invalidate hundreds of years of practice by some of the greatest combustion experts in history from Sir Humphry Davy to Professor Irvin Glassman? We will also get into that.

As a result, writer argues that his strong opposition to G 124-2010 (and now 2018 also), whether he is ultimately proven correct or not, are not casual nor frivolous but is grounded in this rather substantial background of pertinent experience from within a community of rather highly qualified peers, based upon the teachings of outstanding experts, and seeks only to apply the same time-honored thought processes that are applied to the measurement and use of fire limits with other materials. Intuition is not a valid censor for them.

Thus endeth this *voir dire*.

"An Analogy to Something Familiar"

ASTM Committee G4 is in most ways impressive. They represent a large fraction of all the oxygen experts on the planet (regardless of whether it is flat or round). So why would so many in the committee, especially so many in its key cognoscente, adopt a cavalier position dismissing common practices on burn-length criteria, unless it is indeed perhaps viewed, as I once viewed it, myself, as a trivial intuitively obvious issue. An issue so obvious that it does not warrant the normal scrutiny that negative ballots would command, notwithstanding the great complexity that combustion often presents. Why bother to address one nay-sayer.

And if that be the case, then it would clearly not be, and has not been, something easy to challenge. So this writer is going to try to suggest an analogy to something that is equally intuitively obvious, but that is also more easy to understand and analyze with simple equations.

Once upon a time, atomic structure was modeled solely on an analogy to the solar system. Today, some things, like similar quantum mechanic models, for example, do not describe well in terms of an analogy to something familiar. But this is to argue, and to hope, metals combustion is not one of them.

The ignition and combustion of metal specimens has not been reduced to simple nor even complex definitive equations. In coarse terms, when one ignites a metal specimen they are in effect locally widening its fire limits. The specimen may then experience a transient (ignition sustained) burn while consuming and dissipating the ignition energy, until it "burns its way out of the ignition-influenced region", which is to say the region of widened fire limits. This is precisely what Sparks et al. [6] sought to measure, but which this writer argues *they did not*.

Keep in mind that while the metal is burning along, the ignition energy may also be moving with it, and induced combustion of the specimen may sustain and protract the igniter's influence. The metal may not exhibit its native fire properties until this extended ignition energy has been spent. Only then might it burn if it is above its fire limit ...or extinguish if it is below. This aspect was not addressed in the Sparks et al. [6] experiment.

Kick a Can Down the Road

Among past efforts to defend historical fire-limit approaches, this writer compared the ignition and combustion of metal rods to literally "kicking a can down the road." ...There are many corresponding behaviors between them, and while it may seem gut-obvious to conclude a short burn criterion is valid, viewing it from this analogous perspective that can be diagnosed simply and mathematically, may help illustrate why the obvious perspective *is nonetheless wrong*.

So let us kick a can down the road.

When you place a block on a surface, as shown in Fig. 13, basic physics teaches that

Before kick

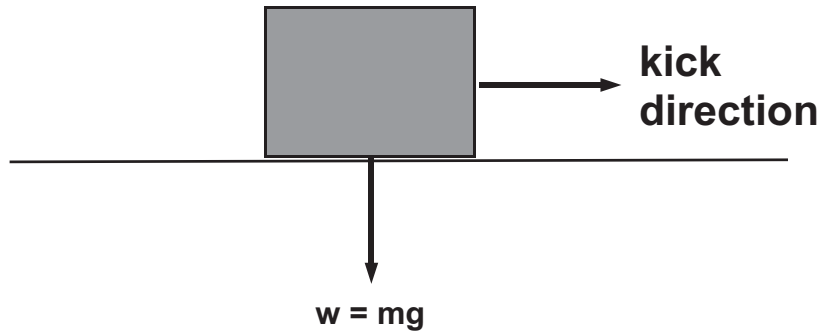


Fig 13—Can on road.

it presses downward with its weight, $w = mg$, the product of its mass, m , and the local acceleration due to gravity, g .

Any attempt to kick it to the right with a constant force F_k can result in sliding movement in the direction of the kick force, F_k . This kick force adds energy to the block and launches motion the way an igniter adds energy to a specimen and launches combustion. This force would produce an acceleration, a , where $F_k = ma$ and therefore by basic physics, for a kick time of t , the velocity would be at , and the displacement would be $at^2/2$.

That movement is countered by a sliding friction force, F_f , acting in the opposite direction of movement, given as the product of the weight of the block and its coefficient of friction, k_f (Fig 14). This force is sucking energy out of the block much the way heat transfer sucks thermal energy out of a G 124 test specimen.

Hence the resultant force acting on the block is the difference between these two forces, $(F_k - F_f)$ and is equal to the mass of the block times the acceleration, ma .

If the kick force is constant, then acceleration is constant and one can easily integrate acceleration to get a velocity, v , and then integrate that again to get can travel, Fig 14.

And so velocity and travel graphs during the kick, look like Fig 15. On the velocity graph, velocity increases linearly with time during an assumed 0.1-second duration kick. On the distance graph, a parabolic increase in distance results with time. A metals specimen test is combustion being kicked by the igniter. As the igniter kicks, the specimen combustion is produced and the combustion velocity and amount burned grow.

When the can velocity exceeds the kick velocity, the contact of the foot with the can ends and there is no longer a kick force being applied. This is akin to a molten droplet falling away that carries all of the igniter fuel with it (even though that is a highly unlikely sce-

With sliding friction

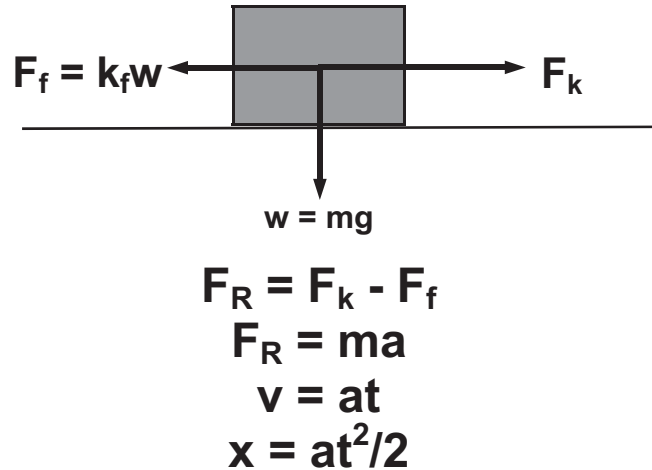


Fig 14—Can with friction.

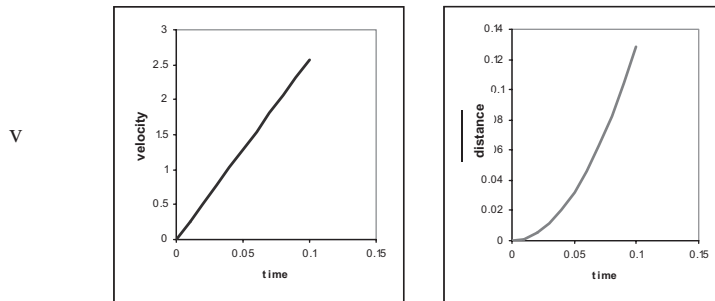


Fig 15—Plots of can motion during kick with friction.

nario). This analogy will prove that when the kick contact ends, when the droplet falls, the influence of the kick, the ignition, *is not nearly over*.

At this point the resultant force diagram on the can is like Fig 16. Only the friction force is still operating, and that is only while the can is moving. The equations estimate the velocity, v_k , and displacement, x_k , after the kick ends at t_k .

So now graphs of the equations look like Fig 17 and the time subsequent to the kick ($t-t_0$) is of interest. The can is moving to the right but the resultant force is to the left and so the can is decelerating.

And the combined curves are shown in Figure 17. We kicked the can, and it moved. Notice the kick launched the can giving it velocity and then the can velocity could not be sustained and decayed to zero. This is much akin to the works of Sparks et al.[6]. They ignited, (they kicked) a rod that was not capable of sustained burning and when the slag droplet fell away, they concluded the "kick" was over and they calculated how far the stimulated

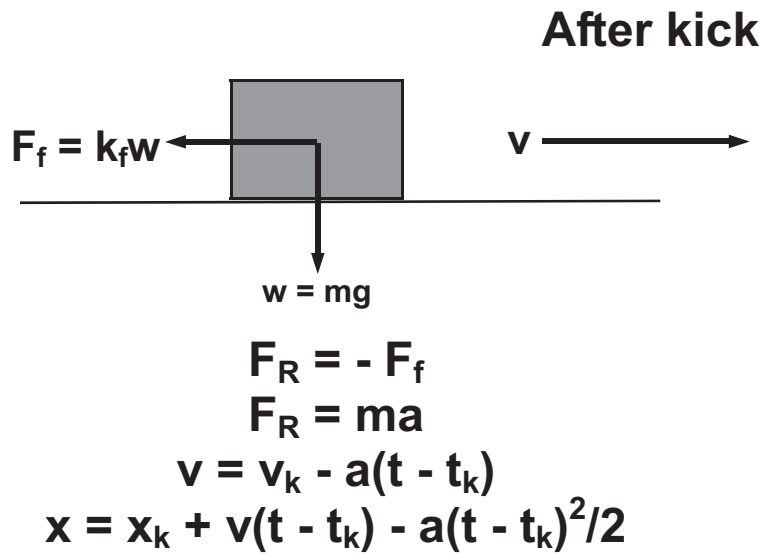


Fig 16—Can after kick ends.

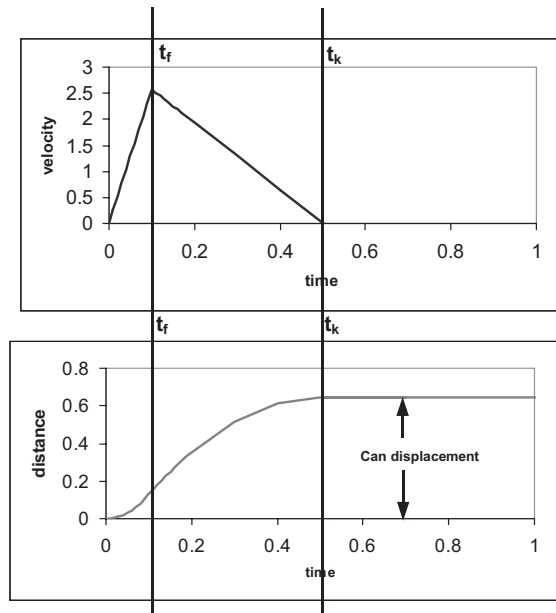


Fig 17—Plots of can motion after kick ends.

(ignition sustained) combustion might proceed (factoring in three sigma and adding a 50% safety factor). They estimated the maximum travel at point (t_f).

Anything beyond this with a real specimen they declared would be "self-sustained" combustion. If a rod were capable of burning beyond this limit then they concluded it might burn indefinitely.

Keep in mind with our kicked can, as with their nonflammable copper rods, the can

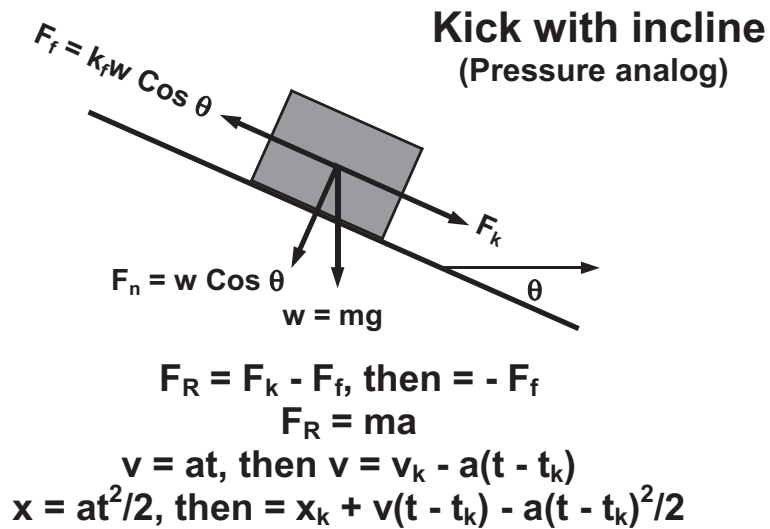


Fig 18—Can on incline, Consequence 1.

is contributing nothing to the motion. With metal specimens, we know both the igniter and any rod combustion are both functions of the oxygen pressure. In the vast majority of cases, (higher pressure) = (lower fire limit).

So in our analogy we are going to relate pressure to surface incline as shown in Fig. 18. When pressure is increased, the igniter burns more easily, more rapidly and possibly more completely. The ignition is typically more powerful at higher pressure. Similarly, the kick of the can is more powerful at greater inclines.

Notice one consequence of this on Figure 18, that the incline reduces the perpendicular (normal) force, F_n , of the can against the road surface by the factor $\cos \theta$. Hence there is less friction force opposing the kick force. The kick will produce a greater velocity and travel distance. The equations change as shown.

Now here is where the fly hits the ointment.

As a rod burns it adds heat of combustion energy to the system, and similarly as the can slides downhill, it adds potential energy conversion to the system due to its decreasing height. Both effects are analogous.

Fig 19 exhibits this second and more important consequence of the change, namely the applicable diagram and equations showing a new force parallel to motion, F_p , having a $\sin \theta$ dependence on incline (the pressure analog).

And Fig. 20 shows the final curves incorporating both effects. Since combustion and incline both add energy linearly, these curves exhibit how kicked distance (analogous to burn distance) results when linear amounts of energy are added. The previous curve for zero incline and zero-incline plus-increased-kick (or ignition) energy due to incline (pressure) are shown.

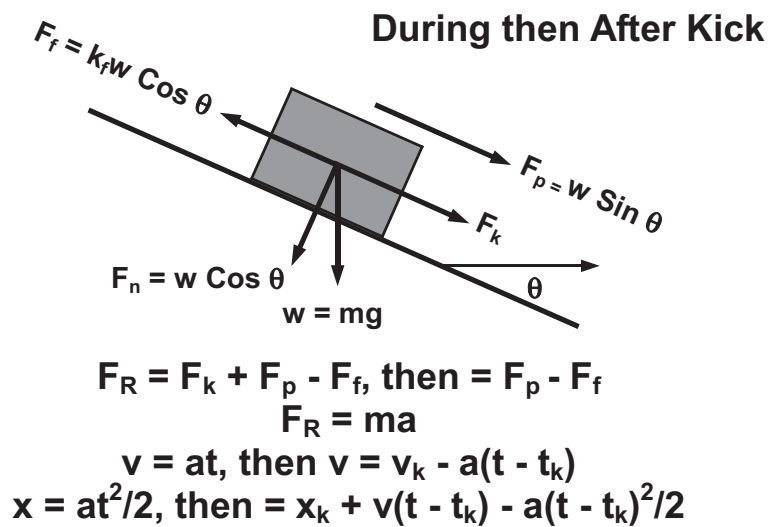


Fig 19—Can on incline, Consequence 2.

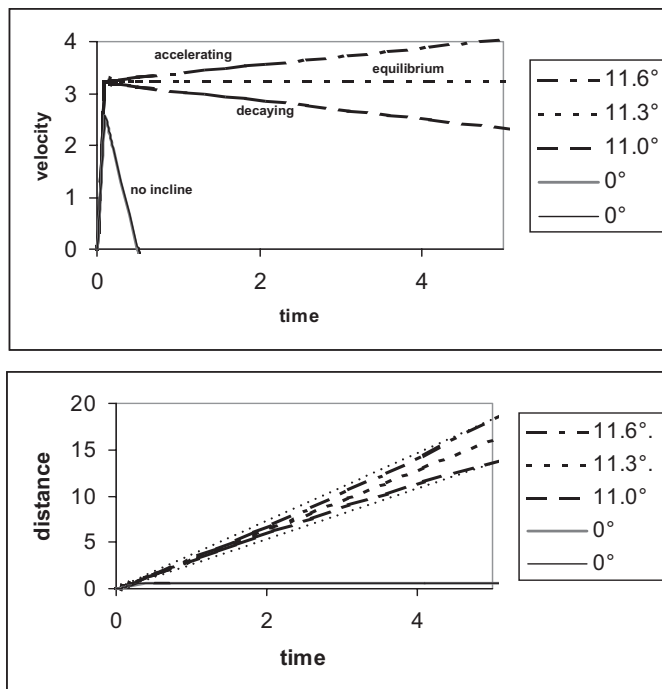


Fig 20—Final distance and travel curves.

Notice that at 11.0°, 11.3° and 11.6°, which include energy added due to incline, we have three different fates when the kick ends.

On the upper velocity graphs, at 11.0° we have a slow decay in velocity after the kick

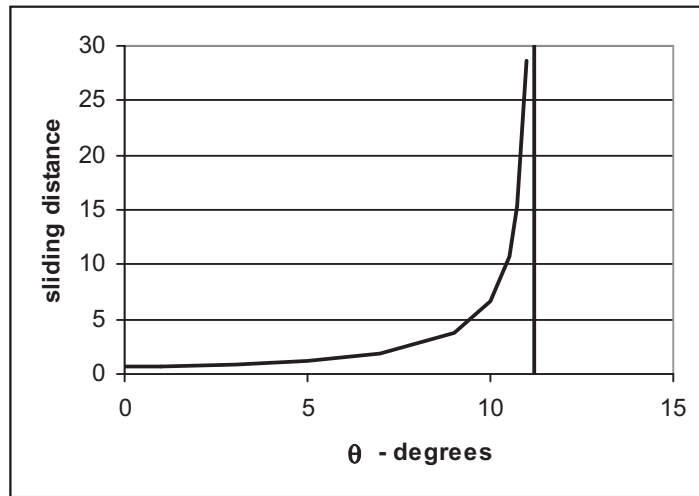


Fig 21—Slide distance versus θ .

ends. At 11.3° we have stable (equilibrium) sliding, and at 11.6° we have accelerating velocity at a low rate. They analogize to being just below the fire limit, at the fire limit (the equilibrium combustion point), and just above the fire limit (accelerating combustion).

On the lower graph we have distance traveled being linear at 11.3° , the equilibrium position, while being slightly concave downward at 11.0° (the decaying position), and slightly concave upwards at 11.6° , (the accelerating position).

At 11.0° , the energy boost of the incline produces a decay to zero velocity that is far off the right side of the chart, and is many, many times larger than the "slide length criterion" that would be estimated if the potential energy of the incline is not included.

So, by analogy, we can *NOT* assume the igniter influence ends when a droplet falls (when the kick ends), because some igniter chemistry may be retained in the surviving droplet, but also because as the rod burns *it adds heat of combustion to the excess heat the igniter may have released* in what Sparks et al [6] call the "heat affected zone"(HAZ). Indeed, adds more heat than the rod alone would add in the absence of igniter heat by virtue of the very nature of an igniter, in effect turning that HAZ section into a second stage, or a spin-off igniter, and it may require numerous droplets to fall, and numerous burn length estimates to be consumed, before the igniter heat has fully dissipated and the combustion reaches true steady-state conditions that may equal or exceed the equilibrium, therefore self-sustaining the combustion ...at which point the only heating is derived from its own combustion.

But what we are interested in for G 124 is the relationship between pressure (or θ) and burn distance (or slide distance).

So Fig 21 is a plot of slide distance versus θ .

Notice how uncannily it looks like G 124 data. At zero θ , a small amount of distance results, in the same way that at low pressure only a small amount of rod destruction results in

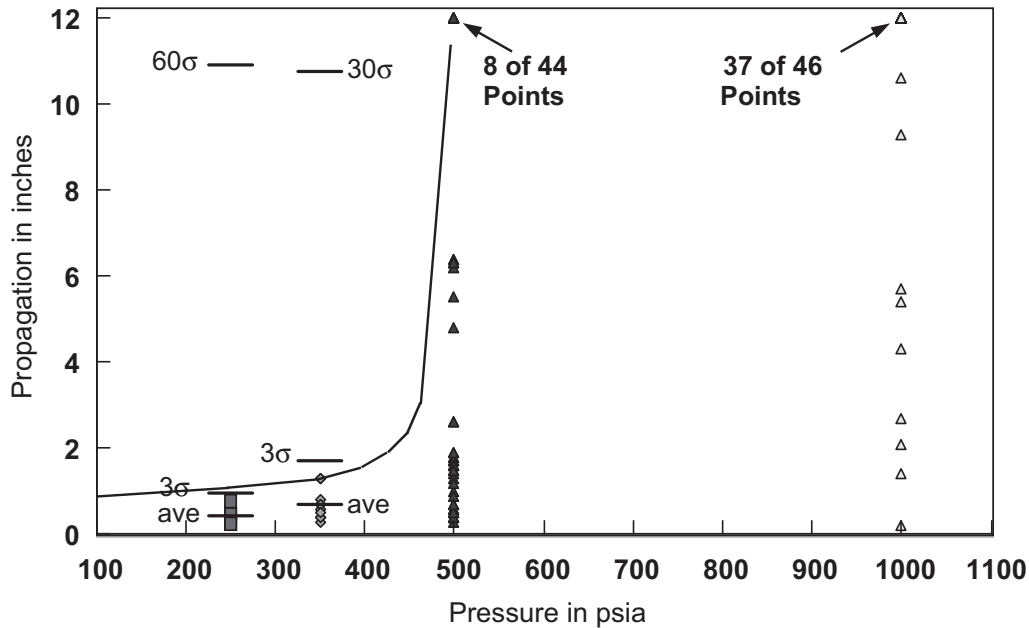


Fig 22—Data from Marshall Space Flight Center [22]

G 124. As θ (the pressure analog) increases, the distance (destruction analog) increases slowly at first then in polytropic fashion curves upward towards an asymptote. The asymptote is the true self-sustaining boundary ... (the true fire-limit analog).

Focus your attention now to Figure 22, the superb MSFC data from Engel, Herald and Davis [22] mentioned before on page 13. How is this for uncanny?

This is approximately the curve they published in ASTM *STP 1479* although the number of test data points for the data Herald provided to the writer are slightly different. This is for 12-inch long specimens. There are roughly 14 points at 250 psig, and 11 points at 350 psig. There are about 44 points at 500 psig and 46 points at 1000 psig. The polytropic curve was eye-ball roughed in for an asymptote of about 500 psig, and it squares nicely with the previous similar curve for the kicked-can analog. The analogy fits pretty well.

Hopefully, this analogy can improve our intuitions about how metals burn. Clearly this can be fine-tuned to even better describe why the current burn-length criteria is not technically correct.

Just a quick word about negative results above the fire limit. Why don't all specimens above the fire limit burn completely as the analogy would suggest? Consider that we can throw in some stochastic behavior that might explain these negatives and erratic extinctions, and elaborate later.

For example, consider a surface that undulates like a sine curve, Fig 23. Perhaps variations in the rate of droplet release can provide this effect. And it at least hearkens to the cyclical behavior we see when a series of droplets forms and fall away in standard tests. If the "effective" (which might mean average, or rms or other formula) slope of the undulat-

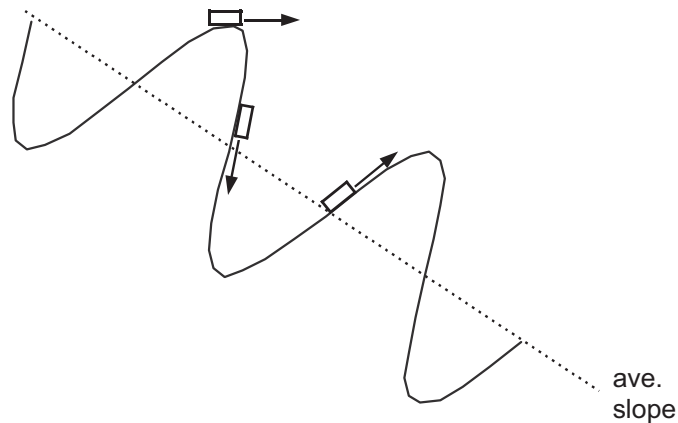


Fig 23—Undulating surface.

ing curve is at the self-sustaining angle then a portion of slide along each cycle will be at an angle greater than the self-sustaining angle and a portion will be at an angle less than the self-sustaining angle. So during a slide it will speed up and slow down (just like combustion of rods does as the droplets fall), and depending upon variations in parameters, it might self-sustain or it might fail. It will sustain if the combustion gains enough or more than enough impetus during the more flammable regions to ride out the less flammable regions.

Something similar results in some G 124 tests. When ignited, many specimens will form a molten slag droplet at the bottom. As it burns surface tension must lift this droplet against gravity until it becomes too large for surface tension to hold it, and then it will fall off. Based on work cited earlier for iron, perhaps that slag becomes too heavy due to its surface tension, or alternatively, perhaps the molten iron droplet within the slag droplet becomes too heavy for its own surface tension.

If accumulating slag inhibits combustion, the velocity will slow as the droplet grows and when it drops off the velocity will increase. A cyclic motion will occur that at any time may dip too far below the self-sustaining condition and may cause a random quench. Numerous other variations in parameters might also cause a quench. And this can help us understand why many tests potentially even a majority of tests near and even above the threshold of self-sustaining combustion may be nonetheless negative.

But this also illustrates the paradox in deciding if an incomplete combustion result achieved some degree of travel because it was kicked there by the ignition energy or because it was above the self-sustaining threshold condition yet somehow stumbled?

As a result, to paraphrase and edit a quote from Sparks et al [6], the writer submits **“.....all metals that burn a distance greater than 30 mm (1.18-in) are *NOT NECESSARILY* burning independently of any promoter effects that preheated the test sample during the ignition process”** (italic text from the writer) and that this analogy, invalidates the BLC adopted in 2010, and proves G 124-10, and therefore the re-approved G 124-18 are not

fit for use.

A Fall-Back Defensive Argument

So far, a working premise has been adopted to the effect that, perhaps the modification of G 124 in 2010, came about mostly because of the previously surmised "intuitive obviousness" of the change. Later it came to be bolstered as the result of an experimental NASA WSTF program [6] designed to specifically measure a "burn criterion" published in ASTM *STP 1522*, that was quite an impressive and ambitious experimental effort, but may have been designed with a presumption, perhaps a conviction, that it would confirm the intuition and this writer has argued it drew its conclusions too soon in confirming the expectation. This writer has concluded the test's conclusions are in error in the previous section.

Advocates of a short criterion have stipulated over the years that it will change the thresholds measured for at least some metals. Nonetheless, a fall-back argument has been voiced, to the effect that even if the test produces a wrong result, that *THAT* wrong result would be equal or lower and therefore conservative and will just lead to even safer systems. In the writer's judgment, this too is in 180-degree error.

So Is it Conservative?

Is this a mountain from a mole hill? A distinction without a difference? Not so! The writer may be a solitary voice within ASTM Committee G-4 taking this maybe not-so-brash-after-all position and bull-doggedly challenging this change for more than a decade, but he does not feel lonely. He believes he is citing hundreds of years of fire limit study and practices by some of the greatest minds in combustion from Davy to Glassman (some of which he knows and has worked with personally). He thinks he is merely restating what they have taught us and is delighted to be defending what he believes was (and *is*) *their* teachings.

Nonetheless, this fall-back argument has been made to the effect that even if the writer's position is correct, even if igniter influence does not end with the first droplet, even if igniter materials cling to the specimen for numerous drops, even if the fire limit measured is simply wrong,it does not matter because the new criterion provides results equal to or less than the former. This view will be disputed next.

The fall-back is entirely correct ,...if these data are used, as they sometimes are, to select maximum operating pressures for materials already known to be "the most compatible of practical alternatives". But that is *not* the primary purpose of G 124.

The G 124 test is primarily used to rank materials and to specifically define "the most compatible of practical candidates" per ASTM Standard G 88. This is the rub!

First a reduction to gross absurdity. Let's carry the fall-back perspective to ludicrous extremes. One could argue: Why not use an even shorter BLC, even a zero length BLC, and get even more conservative results. In this case all metals would be flammable, none would be useful. Or at the other extreme, we could adopt a mile long BLC, which no metal would pass, and so all metals would rank as nonflammable and we could use all of them.

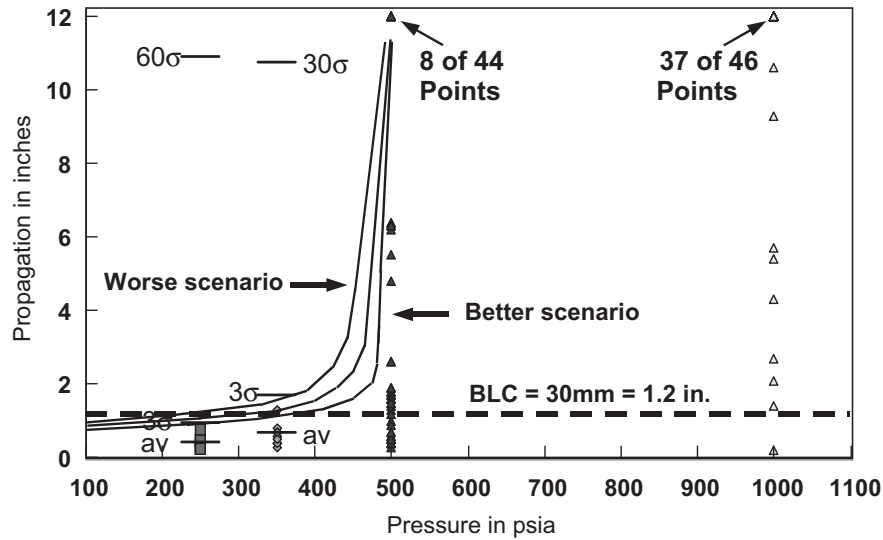


Fig 24—Types of data curves.

Clearly neither extreme meets our needs and so, we must know (via intuitive obviousness) there is a sweet spot somewhere in between. The previous section has shown that 30 mm is *not* that sweet spot. But the situation is much worse when we address G 124's primary reason for existence: relative ranking of metals.

Consider a “hypothetical” figure (Fig 24) here. Well its not entirely hypothetical.

After G 124 was changed over the writer’s perennial protests, in 2010, he obtained these data exhibited in the previous section as Figure 22: the Engle, Herald, Davis data [22]. These were whopping 12-inch long one-eighth inch diameter specimens, of alloy SS 347,... which is a lot like SS 304...it is an 18-8 alloy but it also contains a bit of columbium, tantalum, and titanium. Still the results are consistent with what Zabrenski [17] measured for one-eighth inch 304 and other rods and they also extrapolate nicely to what Zabrenski saw for larger-diameter 304 specimens. Ditto with what Hansel and the writer [18] saw for similar alloys.

Fig 24 is again the writer’s plots of the MSFC data. Now, be reminded again the data provided are not exactly the same set as in *STP 1479* but very close. The writer’s polytropic curve is present and also a broken horizontal line is exhibited as the 30-mm (1.18 inch) burn-length criterion (BLC) of G 124-10. Also shown are two alternative polytropic curve scenarios. A curve marked "worse scenario" because it intersects the BLC curve at even lower, more conservative pressures. Finally a curve marked as “better scenario” because its intersection with the BLC boundary is closer to what will be defended as the **true** fire limit (the asymptote).

To illustrate one way in which curves like these might obtain, Figure 25 is the kicked-can analog distance-versus-incline-angle situation presented before. The middle curve is for a one-pound kick force, the upper curve is for a strong 2-pound kick force and

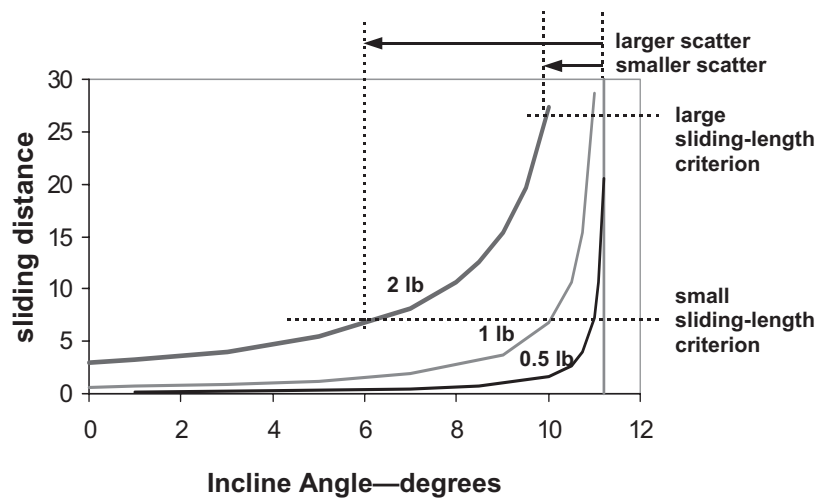


Fig 25—Types of kicked-can data curves.

the lower curve is for a weak 0.5-pound kick force. Since kick force analogizes to ignition energy, this illustrates how a strong ignition (of the kind G 124 uses and needs) can skew the surmised fire-limit when too small a BLC is used. Notice the 2-pound kick has the greatest scatter and the 0.5-pound kick has the least scatter.

Back to the Marshall data.

Notice back on Figure 24, that at 500 psi there were eight complete 12-inch burns in 44 tests. Clearly the threshold is at or below 500 psi, regardless of criterion used.

At 350 psi, there were no complete 12-inch burns nor 6-inch burns in eleven tests but two specimens exceeded the new 1.18-inch G 124 burn criterion at 1.2 inches. How fortuitous for the writer! While the old G.124 would argue the threshold might be as high as the 500 psig value, give or take, the new criterion says it is at or below 350 psig. The writer's 30 year old tests on quarter-inch SS 304 might now argue the 304 threshold of 0.25-inch rods is perhaps hundreds of psi lower than was previously concluded on the basis of Zabrenski's and other massive testing, *but it would be wrong*.

Notice that for the 350 psig data, the writer has shown where calculations of mean (0.7 inches) and upper 3-sigma (three times a sigma of 0.334 inches) standard deviation limits fall.

Notice also that normal probability indicates that to achieve a self-sustaining propagation above the three sigma level would be at a 0.13% rate. This estimates we would see a propagation greater than about 1.18 inches once every thousand tests/accidents. This does not qualify in the writer's mind as exceeding the self-sustaining fire limit. Notice a bar indicates where the 30-sigma level is that would be exceeded for a full 12-inch propagation. One might suspect the odds of *this* happening are approaching the odds of having all the air in the room the reader is in suddenly deciding to go to one corner and leaving you sitting in a vacuum.

At 250 psig, none of the 14 tests exceed 1.18 inches, but they came *very* close. Here again the mean and 3-sigma levels are shown and in this case, the level that would have to be exceeded to experience a 12-inch fire would be beyond the 60-sigma level. Wow! Feel free to check the math.

Does anyone feel oxygen systems must be designed to avoid 30 and 60 sigma events?

So this writer is hereby declaring for the sake of this effort that for these data, the 250 and 350 psig results are *below* the true fire limit and the 500 psig results are at or above the true fire limit.

But because of the number of tests, let us now apply these not-only-realistic but REAL data as typical sets of results. Yes, in real testing the results could bounce around but for the main, these results should be rather representative of typical populations. Let us 3D print some dice that exhibit each test result on a different side. One die with 14 sides for the 250 psig results, one with eleven sides for the 350 psig results and one with 44 sides for the 500 psig results.

We can now cast lots (throw the dice, shoot a form of craps) to simulate testing. We have these three dice. The 14-sided (for 250 psig) die has no numbers on it greater than the BLC, therefore none greater than a 6 or 12 inch length. One 11-sided (for 350 psig) die with two numbers (18.2%) greater than the BLC, and no numbers exceeding either 6 or 12 inches. Both of these sets of data seem characteristically similar to data for repetitive measurements the writer made back in the 1980s (but may have done an even greater number of tests). And the third 44 sided die has 31 sides (about 70.5% exceeding the BLC), and with about 29.5% exceeding the six inch level and about 18.2% exceeding the complete-combustion 12-inch level.

So now we can, hopefully, simulate test series, to estimate result "expectations" at each of the pressures for repeated G 124 test series by simply tossing these dice.

To calculate the probability of positive results (in one or more tosses of the dice), we take the probability of a negative result for a single toss and multiply it by itself for each toss. This gives us the probability of all tests being negative. We then subtract that product from 100% to get the percentage probability of at least one positive result.

ASTM Standard G 124 says to use five tests (five tosses), the MSFC paper [22] suggests using ten tests (ten tosses). Table 1 shows estimates of the errors that result.

Here we see that regardless of the three BLC chosen, whether we require five or ten tests, we "expect" no errors in tests at 250 psig where a "*true*" result is negative.

At 350 psig where a "*true*" result is negative, we expect 63.4% of our test sequences using the 1.18 inch criterion to be in error. And note the curious result that if we do ten tests, the error rate rises to 86.6%. Indeed the more tests we do the worse the error rate becomes because the probability of throwing one of the two sides that wrongfully score as positives grows. But we expect no errors with 6 or 12 inch criterion for either five or ten test se-

TABLE 1—Estimates of Results expectation for “Craps”

Probability of "Wrong" Results			
True Result:	250 psig Negative	350 psig Negative	500 psig Positive
five-specimen test series:			
1.18 inch BLC	0% (+)	63.4% (+)	0.22% (-)
6 inch criterion	0% (+)	0% (+)	17.4% (-)
12 inch criterion	0% (+)	0% (+)	36.6% (-)
ten-specimen test series:			
1.18 inch BLC	0% (+)	86.6% (+)	0.00050% (-)
6 inch criterion	0% (+)	0% (+)	3.0% (-)
12 inch criterion	0% (+)	0% (+)	13.4% (-)

quences.

At 500 psig, where a “true” result is positive, a capitulation is offered the writer had not previously realized even though it is as obvious as the previous insight, indeed as obvious as whether the earth is round or flat. *In this case the short BLC reduces the error rate.* With a five test sequence, the expected error probability is only 0.22% and with a ten test sequence that drops to 0.00050 percent. While for the six inch criterion it is 17.4% with a five test sequence and drops to 3.0 percent with a ten test sequence. And with the 12 inch criterion, it is 36.6% with five tests and drops to 13.4% with a ten test sequence.

Furthermore also by way of stipulation, with a five-test sequence, a 12-inch criterion, causes the 500 psig error rate to increase to 36.6 percent from 17.4 percent at 6-inches. Similarly with a ten-test sequence, a 12-inch criterion causes the 500 psig error rate to increase to 13.4 percent from 3.0 percent at 6-inches .

This again makes perfect sense in that with a longer criterion, specimens are less likely to burn completely, because the rate of failure is the rate of failure to burn 6 inches PLUS the rate of failure to burn between 6 and 12 inches. Hence there must be an optimum criterion (a sweet spot) to minimize errors in both the lower boundary and upper boundary conclusions. But this is actually just a restatement of the earlier absurd considerations of either a zero or mile-long criterion.

This tells us is that if we test Alloy SS 347 a hundred times (that is to say 100 test sequences of five specimens each, at 350 psig) using G 124 and the short BLC then about 63

tests will say it's fire limit is at or below 350 psig (in error) while 37 tests will correctly say it is above 350 psig.

But because we *know* its "true" fire limit is above 350 psig, then 63.4% of the tests at 350 psig are going to wrongfully under-rank SS 347.

At the same time any similar metal with a true limit between 350 and 500 psig, and therefore LESS compatible than SS 347 would be expected to produce a "true" negative result at 350 psig in perhaps something between 0.22% and 36.6% of the test series. Therefore these data would point you to use of the less compatible metal perhaps up to ~63.4% of ~0.22% up to ~36.6%, or between ~0.14% up to ~23.2% of the time. G 124 will tell us to chose to use the less compatible metal as much as one in four times because of this high error rate. Because of this under-ranking, G-4 standards will direct you to use a less compatible metal instead of the "most compatible of practical options."

A more thorough and competent study of these statistical possibilities would be worthwhile. Are there offsetting aspects?

Note that with the ten-specimen procedure of MSFC, using the 1.18-in. BLC, a false positive for SS 347 at 350 psig is expected in 86.6% of test series, but that when compared to a less compatible alloy with a limit between 350 and 500 psig would multiply against a true negative range of 0.00050% to 13.4% for a range of these rankings of 0.00043% to 11.6% of the test series.

Note that with either the 6 inch or 12 inch criteria, the error rate at 350 psig would be zero, and alloy 347 would not appear to have an erroneously lower fire limit.

Hopefully this approach has not grievously offended any statisticians (but it might have). And there may be many other issues involved here that someone better versed in statistics might take issue with. But the goal of G 124 is to avoid this sort of thing by giving clear methods to rank metals.

So now the writer can only hope he has adequately argued the short BLC does not *always* yield conservative results. So what!... So what if we don't use the most compatible of practical materials. So what... if we have a fire and an injury results. So what?

Court Testimony and Plaintiff Craps

This controversy may fall into a category of where we can only agree to disagree. The argument here, make of it what you will, illustrates how the current 1.18 inch BLC can yield wrong results, the example metal was wrong >63% of the time with a low result. The example showed how wrong metals may be chosen as much as >20% of the time or more.

Fires happen!

Lawsuits happen!

And when one has an accident with the "wrong" metal, what if one finds themself on a witness stand. Plaintiff's attorney refers one to the G 88 ethic "*Use only the most compati-*

ble of practical materials and designs” and asks one if a more compatible alloy might have spared the client. No brainer! Yes. More compatible materials do tend to reduce fire risk. "So why didn't you use the more compatible alloy SS 347, and at least give the client a chance at a normal unscarred life or maybe even allow the client to live a longer life.

Your honest answer: Because the test you used to rank the better SS 347 is wrong on the low side >63% of the time and gave a wrong result, while a lesser material that is right >30% of the time gave a correct result. The dice you rolled on his behalf came up craps for him. The injured is a victim of bad luck. Can anyone hear the corporate cash register going: Ka-Ching?

Hence, when two sets of data rank metals differently, how does one use two practical metals that formerly ranked one way and now are reversed? Must historical systems be re-evaluated and retrofitted? Do repairs to systems mix old metal choices with new? Can old test data for one metal be ranked against new test data for a different metal? Must all metals be retested? And how would examples like these be defended in court following an incident?

Compromises, Capitulation, Modifications

The key points of this saga have now been made. You can skip to the final summary and be done with it. However, a few additional opinions may be in order on how and why specimen testing may be so onerous, and to recall and to elaborate on both some alternatives proposed in the past to deal with the onus and to offer some new suggestions.

A capitulation has been offered to the effect that the terminology "complete combustion" is not "literally" the ideal criterion to use in G 124, even though a valid BLC for historical specimen sizes (up to 6-in.) is tantamount to their complete combustion. Instead, "equilibrium or greater combustion" is and always has been the precise arbiter of self-sustained combustion but so far traditional methods of metals burning has not been able to achieve the needed observation capability. However, when testing three inch and probably also six inch specimens, complete combustion is largely adequate if not optimally efficient. However, the 2010 BLC of 1.18-inches (30-mm) is simply way too small.

Having condemned G 124-10, one can nonetheless sympathize with the desire to validate a burn criterion alternative to "complete combustion". The writer has attempted to suggest alternatives in several past negative-ballot defense statements (suggesting the use of windows, X-rays, ultrasound, etc,) and refers the reader to them for details. They were all approaches to better observe a specimen's combustion directly or instrumentally so that better judgment is possible. A different tack is offered here in an attempt to improve test behavior and thereby to reduce erratic extinction results

Standard G 124, exposes specimens to at least four mechanisms that must be kept in mind during testing and perhaps should be revisited in light of today's technology. Doubtless many other mechanisms may be entering into any erratic extinguishment, or not, of these

specimens. And indeed, using the approaches of G 125 Section 12 (on Interpretation of Results) and of oxygen index testing and gas fire-limit testing would all be helpful to apply, as soon as technically possible to implement today. But the writer would like to remind you of a few mechanisms that might especially aggravate undesirable scatter in test results from using the present G 124 procedure with an optimum burn criterion:

1. **Pressure Induced Scatter.** G 124's sealed vessel exposes the sample to an increasing then decreasing ambient pressure as the gas is heated then cooled and consumed. This causes decreasing then increasing dynamic fire limits during a test. This is undesirable. Constant pressure is preferred. Zabrenski's [10,15] testing employed a flowing system that helped control pressure swings. Early on (1980s), NASA WSTF experimented with large ballasts, to damp pressure swings, but an active pressure controller might be able to bleed off increasing pressure and a forward pressure regulator used to back-fill decreasing pressure and perhaps should be revisited.

In addition, the pressure swing might be reduced by including a copper cooling coil or finned surfaces to impinge the hot combustion gases onto and to drip the slag onto to quickly cool it and quench it, and reduce or prevent so much heat-exchange to the oxygen inventory. This seems easily do-able.

2. **Purity Induced Scatter.** G 124's non-flowing system allows depletion of oxygen and increases of impurity levels up to a bulk ten percent. But impurity-rise greater than 10% locally... in the combustion zone...is possible. Alas, in too many works, oxygen is called out only as 100%, something it most certainly never is either during the test nor even at the outset. "Oxygen" of aviator breathing or commercial, zero, electronic or other grades, has initial purity that varies significantly in the region between 99.5% and 99.9999%. And before and since the fledgling introduction of G 124 in the 1990s, commercial oxygen purity has on average increased in a fashion that can exhibit increased scatter in the actual purity and therefore on the measured fire limits of some metals albeit a much smaller effect on the metals of most interest here, but still with a similar and significant effect on burn velocities even for these metals. Better purity control also seems straight-forward to do.

3. **Bulk Temperature Scatter.** In a closed vessel the bulk gas temperature tends to rise and then fall more slowly just as pressure rises and falls, and for the same reasons,... again messing with the local fire limits. Correcting effect one, above, also helps with this effect.

4. **Local Temperature Scatter.** Convective and conductive heat transfer effects are present and perhaps most critically important of all, and much harder to describe here but may not be so hard to remediate. So the remainder of this chapter will focus on this aspect.

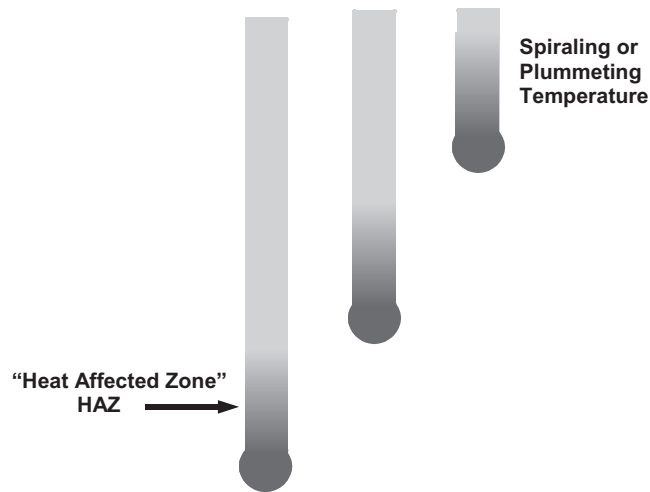


Fig 26—Heat-affected zone approaching specimen end.

Heat Transfer Effects

MSFC data [22] have been invaluable to this analysis. They have enabled statistical calculations. They have illustrated why very long "complete burn" criteria can protract testing unnecessarily. They have allowed test series sizes to be examined. And on a personal note, they have given the writer confidence in his own testing of some two decades ago.

The writer's analyses of 2002 [3], 2010 [2] and 2014 [1] examine many of the issues surrounding erratic test results. This final section will elaborate and expand upon just one of them: convective heat transfer effects, specifically as they may be influencing the scatter in MSFC test results (and therefore maybe all the other data out there).

In the 1980s, John Zabrenski tutored the writer on what he called heat accumulation. When a specimen burns, it transfers heat into the remaining specimen (akin to what Sparks et al later [6] called the Heat Affected Zone). As the specimen burns, the heat affected zone is passed upward into the remaining specimen.

As the combustion zone approaches the end of the specimen, Figure 26, the holder will either drain the heat energy at the same or a lower or higher rate than would a longer specimen. For many holders, the conductivity will be small and so the heat wave approaching the end of the specimen will "accumulate" (pile up and reflect off the end and cause the temperature rise-rate to increase), and thereby lower the fire limit of the very end section. This will abet combustion to burn up to, or even into, the holder.

On the other hand, if the holder is very conductive and beefy, as the combustion zone approaches it will draw off the heat transfer, cool the combustion more than a longer specimen would, and may cause the specimen to quench before the combustion gets all the way to the holder. This is why the definition of self-sustaining combustion in the original G 124-

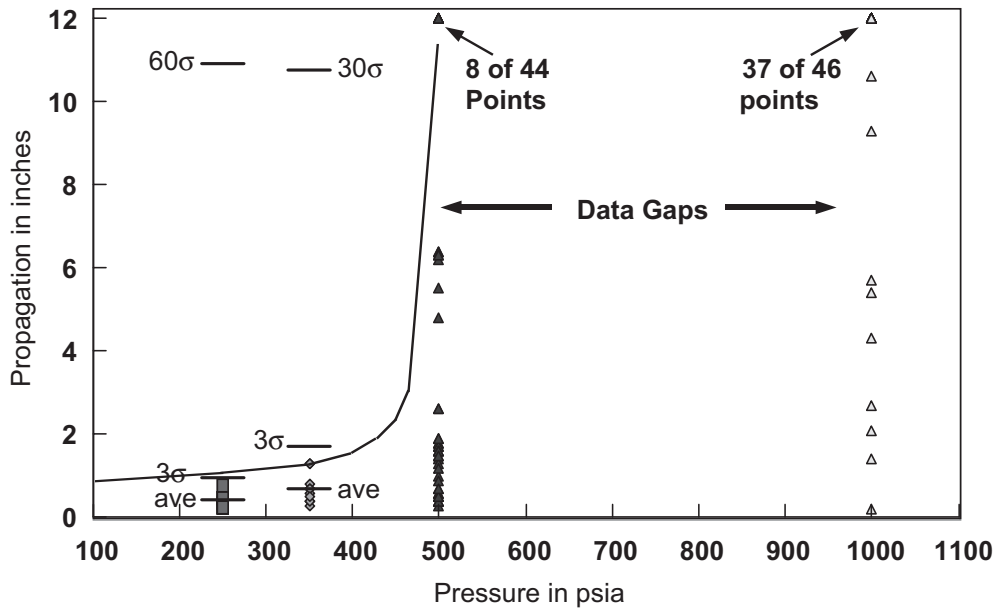


Fig 27—Gaps in MSFC data.

94 was combustion to the point where the holder interferes with that combustion.

Indeed, there might be merit to simply considering the top portion of the specimen itself, perhaps one heat affected zone (such as the Sparks et. al. [6] 1.18-inch estimate) to be a part of the holder rather than part of the specimen so that this effect can be minimized.

Next one can argue that a convective heat accumulation was operative in the burning PTFE tests mentioned earlier in this paper (Figs. 7, 8) and also in tests under G 124. Convection mechanisms may be, in fact probably are, operative in the MSFC and other apparatuses. Recall the SS 347 data again shown first in Figure 22, and repeated in Figure 24.

Notice in Figure 27, the two gaps in the 500 and 1000 psi results between roughly 5-7 inches and full combustion. In the original figure, the gaps are also present at some other pressures and less obvious at still other pressures that are not shown. This hearkens back to a critical boundary as the writer previously observed for PTFE combustion in Oxygen Index testing (Figs. 7, 8)). Notice that few results fall between 6 and 12 inches. If the combustion can get to the 5-7 inch critical point, then it tends to go all the way. This is not the way normal statistics would predict.

This same behavior was previously described in oxygen index testing of PTFE when the convection patterns in the apparatus flipped and, instead of purging combustion products up and away, suddenly bathed them down onto the lower regions of the specimen thereby facilitating complete combustion.

This begs a suggestion that convective heat transfer is doing something similar in the MSFC system. And it may be due to a form of heat accumulation.

Recall that when we kicked a can, the energy produced some sliding motion. Any

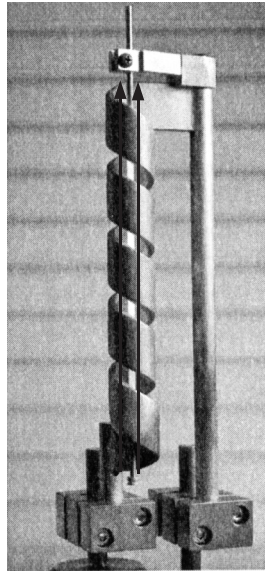


Fig 28—*MSFC specimen holder and induction coil* [22].

added incline then magnified the motion.

Engle et al [22] provide the photo in Figure 28 for their 12-inch system and its induction coil.

Note that specimen ignition at the bottom will result in a buoyant rise of hot gases to heat the specimen above (in combination with conduction but moving much faster). The buoyant gas paths are shown with vertical arrows on Figure 28. Indeed, the induction coil although of spiral geometry will also tend to channel and baffle the hot combustion gases upward rather than allow them to disperse or be blown laterally.

Be advised in the metals testing the writer has observed, in the vessel of Figure 29, in which there was an overhead window, upon ignition an almost immediate rush of gases plastered the window with debris. The upward convection currents are quite impressive supporting the claim that the upward currents move at a velocity much faster and further than conduction provides. And although a downward flow of oxygen was used in this vessel, its average velocity was much less than for these localized upward draft currents. The original intent back then was to sweep the combustion heat out the bottom to duplicate oxygen index testing in which heat of combustion is swept upward and away by both bulk flow *and* buoyancy. But it did not work that way at the nominal gas flow rates used.

In developing the oxygen index test [23], GE Research tried four configurations (Figure 30): Top (candle-like) ignition of vertical specimens in both upward and downward oxygen streams, and bottom ignition in both upward and downward flowing streams. They chose top ignition with upward flow, the first configuration shown, even though it was not the most flammable configuration, but because it gave the most reproducible and well-

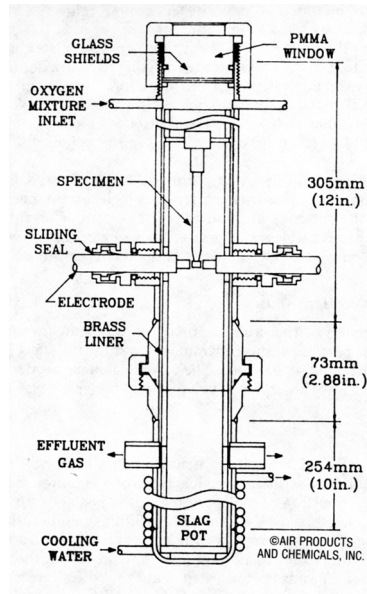


Fig 29—Vessel of writer's experience [17].

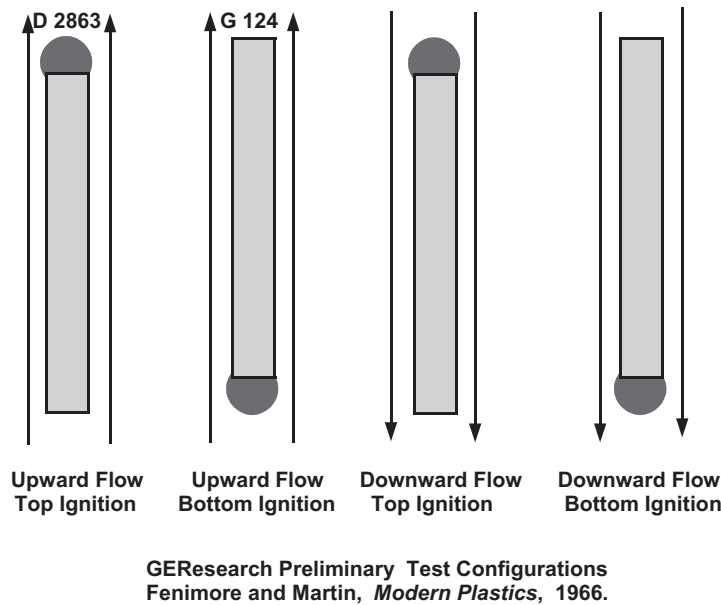


Fig 30—GE Research preliminary test configurations..

behaved results rather than, for example, top ignition with downward flow. This was at least in part because most polymers (with a few exceptions) do not drip in the test, they burn like candles, and those that do drip are a real mess to test and interpret.

But the Oxygen Index test was not intended to identify the most flammable scenarios. To increase flammability, one can granulate or even powder the material which can make either polymers or metals explosive. Oxygen Index tests were intended to measure *relative*

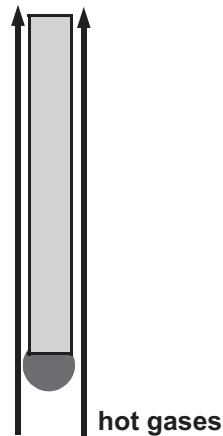


Fig 31—*Path of hot gases.*

flammability as a quality-control test, much in the way they are used to compare and rank flammability in G 124.

So when the writer's group began metals testing they opted for bottom ignition, because many metals do drip during combustion and bottom ignition allows the droplets to fall away from the specimen and avoid increased preheating, and even worse, "lighting of the candle at both ends and burning towards the middle". And that enabled an equilibrium combustion mode to be measured. Hence a downward flow to carry the hot gases away similarly was selected. However, the power of the upward convection currents was misjudged and so one of the goals was not realized. Nor did G 124 solve this issue when it came along with a stagnant initial gas.

Furthermore, back then, these data were a major leap forward. But maybe the state of knowledge is better today and suggests a need to reexamine the test.

Since G 124 does not employ even a nominal bulk flow, it must suffer even more so from the buoyant hot-gases heat transfer. Hence it is like the second example of Figure 30.

In fact what we have in G 124, and more so for the MSFC long embodiment, is an undesirable counter-current heat exchanger which caused so many problems in the development of the standard oxygen index test.

To an observer on the specimen, it moves into the flame zone while the combustion gases move up the specimen Figure 31. Upon ignition, the fast-rising hot gases begin warming the entire length of the test specimen. Conduction only warms it near the molten droplet.

In principle, every successive increment of a specimen that burns will have been exposed to a greater amount of convective heat transfer than was the previous increment. Each increment will therefore have a lower incremental fire limit. It is like kicking a can down a hill that curves downward...will the friction drag it to a stop before the slope crosses the "self-sustaining angle"?

This may almost guarantee an equilibrium process is not achievable, because each

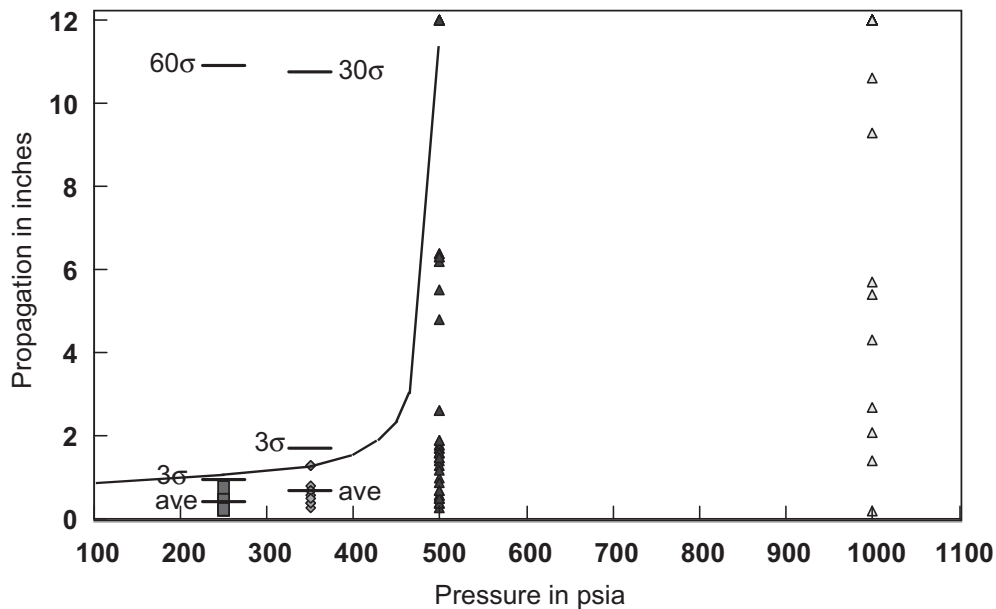


Fig 32—MSFC Data repeated [22].

element of specimen that burns may be... inherently... at a higher temperature.

When we use a complete combustion criterion, we may be measuring approximate, but low fire limits in which we are kicking the can down the hill and scoring the fire limit as the transient combustion scenario for which it will just burn the length of specimen we are using.

Sooner or later, the hot rising gases even those from transient combustion will "counter-current" heat the distant specimen regions above where their fire limits will be lowered, and then more certain combustion and even accelerating combustion may develop.

When the combustion reaches the 5-7 inch point in the MSFC apparatus (Figure 32), it appears to cross just such a boundary. Hence getting to the half way point may greatly increase the odds of a complete combustion...just as we see happening in their data, Figure 32.

In the can-kicking analog, equilibrium sliding occurs when the component of force produced along the surface equals the friction force in the opposite direction. Figure 33 shows three differing coefficients of friction and the *matching* slide angles at their equilibrium asymptotic limits.

If we were to have a can warm up as it slides, and if it had a lower coefficient of friction when it was warm (the way a burning specimen has a lower fire limit when it is warmed), the slide test could start out where the dotted arrow does on Figure 33, at a 0.3 CoF, below the limit, and shift to higher curves above (lower friction coefficients) ultimately reaching a critical point at the limit

Zabrenski [17] did testing, Figure 34, with inclined specimens (*STP 1040*, p. 178)

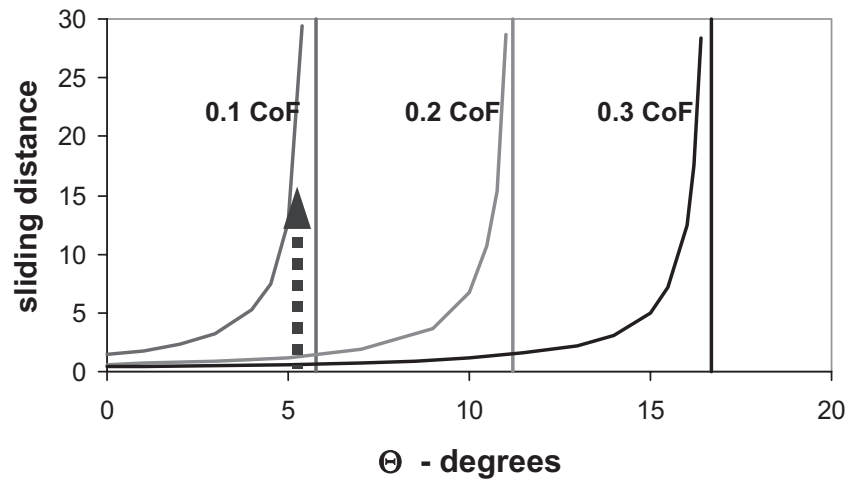


Fig 33—Kicked-cans of varying coefficient of friction.

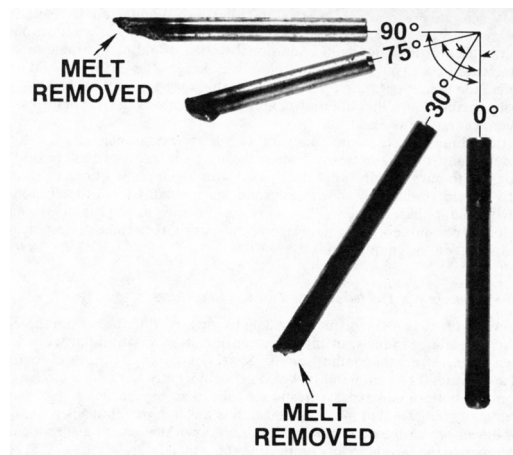


Fig 34—Zabrenski's inclined specimen tests, STP 1040, p. 178 [17].

and did indeed report that the lowest thresholds were found with vertical specimens. These tests were intended to study the effects of slag drainage, because many workers believed slag interferes with combustion, and so if the slag can drain more readily it was feared greater flammability would result, but that did not happen. That effort did not focus on convective heat transfer effects as a possible explanation for the minimum limits in the vertical position. It might be worthwhile doing that today.

To milk this point further, note that the inclination of a specimen would hugely affect the degree of coupling of the buoyant gases with the upper part of the specimen and could be a major source of scatter in results.

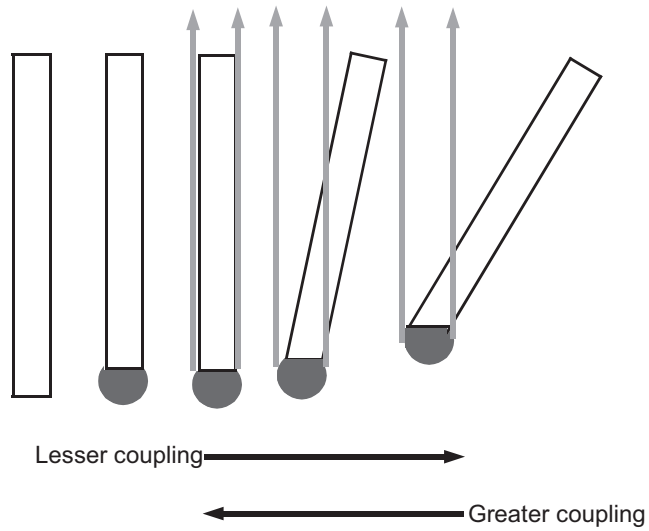


Fig 35—*Geometrical heat coupling.*

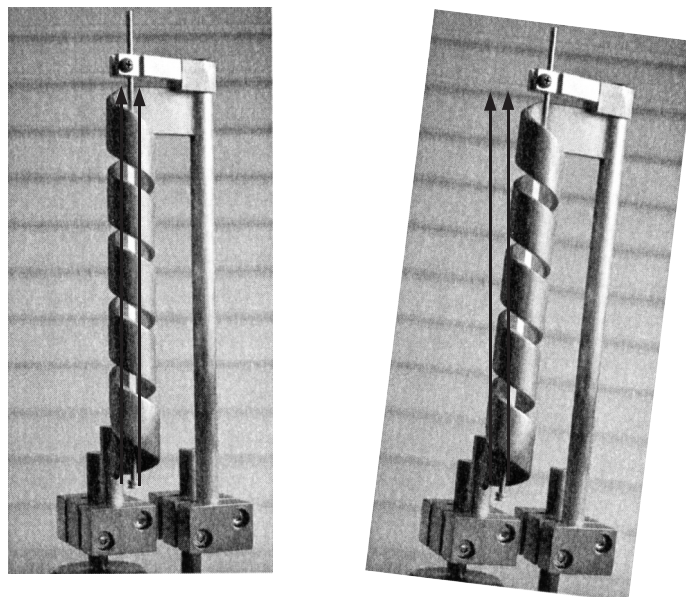


Fig 36—*MSFC vessel with specimen on and off plumb.*

Notice in Figure 35, how a plumb specimen is ideally positioned geometrically to transfer heat from rising gases. A significant incline can almost totally decouple such convective heat transfer.

In the MSFC system, Fig. 36, even a small deviation from plumb, as shown, might

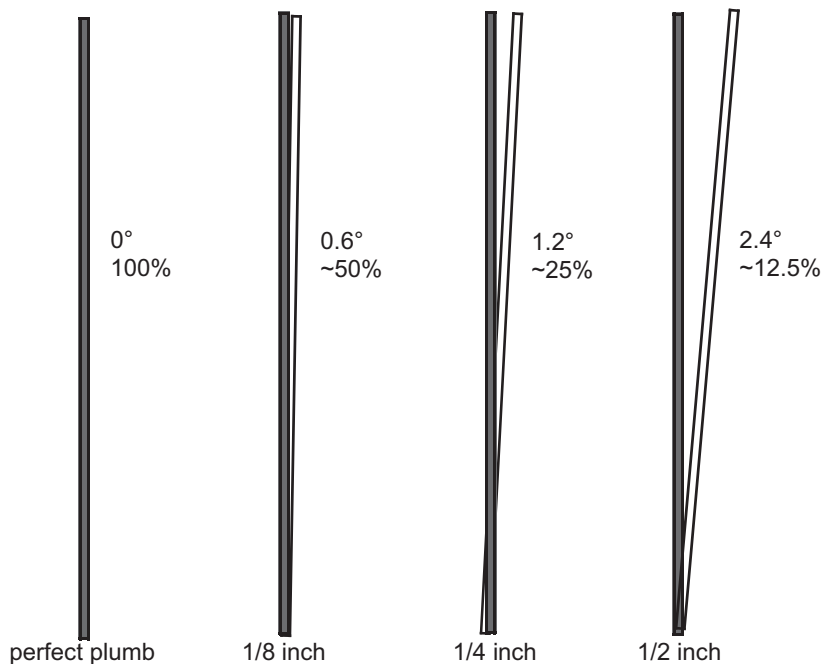


Fig 37—*Effect of variations in plumb on geometric coupling of heat transfer.*

affect distant preheating of the long specimen. Hence random small variations in specimen plumb might account for some of the scatter we are seeing,

Figure 37 shows how the geometrical coupling would vary for the MSFC small diameter 12-inch long specimens. Notice even just 0.125 inch of misalignment at the bottom can make a big difference in geometrical coupling (50%) and maybe account for some of the undesirable scatter typically seen.

Does this suggest that perhaps a slight incline would not elevate the threshold greatly due to slag drainage issues and the decoupling of the buoyant hot gases might thwart distant heat transfer and maybe also prevent the critical distance effect just surmised,..... if it proves valid?

Figure 37 suggests a 0.125 inch error in plumb, results in a reduction of geometric coupling from 100% to about 50%, but adopting a standard offset of just 0.5 inch would geometrically decouple nearly 90% of the buoyant gases. If this effect is significant, it should produce much better behavior from the data.

Figure 38 shows how a beefy metal plate, perhaps finned, perhaps water cooled, located just above the specimen can allow much of the hot gas to quickly cool before mixing into the bulk oxygen and increasing both its pressure and temperature...both also desirable.

Furthermore, Figure 39 illustrates how with a vertical specimen, successive droplets fall onto each other and accumulate to produce a compact (low surface-area-to-volume) slag. With an inclined specimen, each slag droplet could fall to a displaced cooler location on what could be a beefy copper (perhaps finned, perhaps water cooled) slag catcher and should

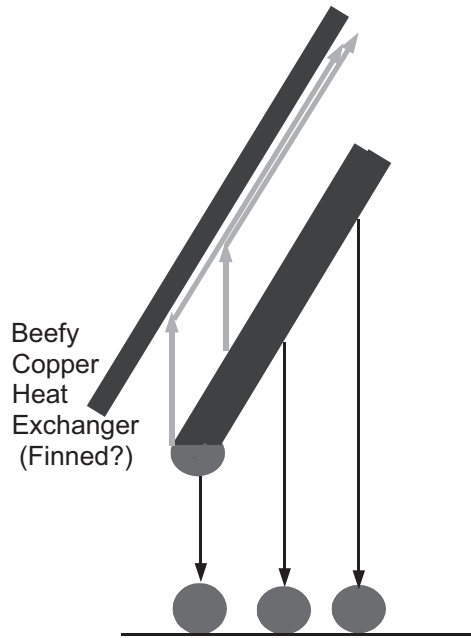


Fig 38—Interception and cooling of hot combustion gases..

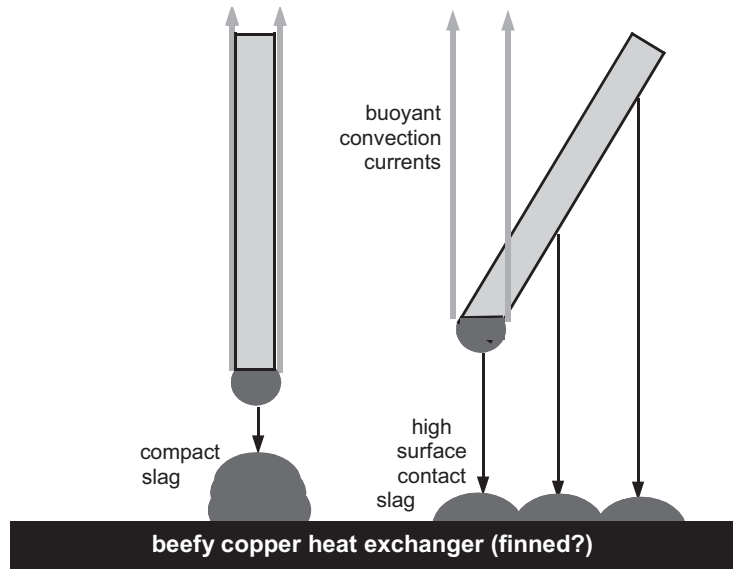


Fig 39—Use of heat transfer surface to quickly cool hot slag droplets.

cool the slag and quench any after-burning to also reduce heat transfer to the gas leading to less ambient oxygen heating, less local oxygen purity decay, and therefore less temperature and pressure rise. All of this being more good stuff in the writer’s opinion.

Figure 40 illustrates how an actually might behave.

Finally, perhaps a pressure snubber should be considered as in Figure 41. Whereas a ballast vessel as tried at NASA WSTF, requires the same volume as the test vessel to produce a 50% cut in pressure rise or fall, any given rise or fall can be eliminated with a smaller sized snubber-volume change. And indeed, the data published by labs with flowing systems

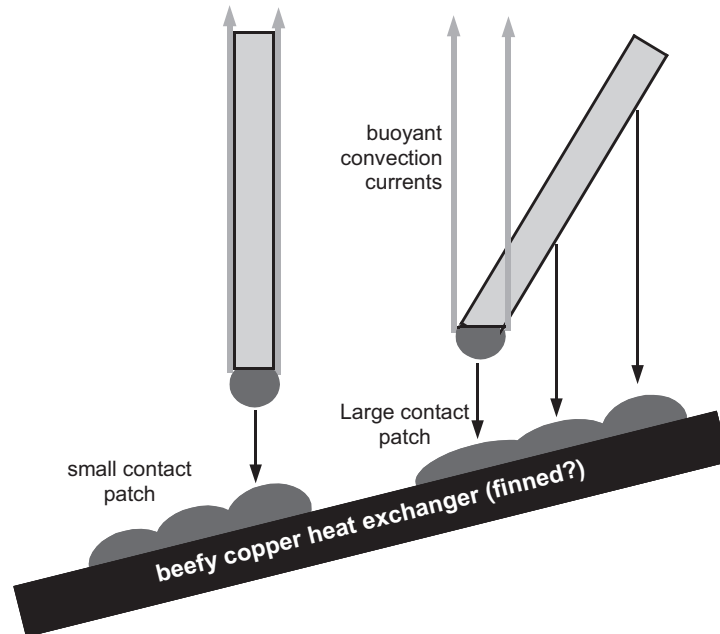


Fig 40—Benefit of inclined heat transfer surface to quickly cool hot slag droplets.

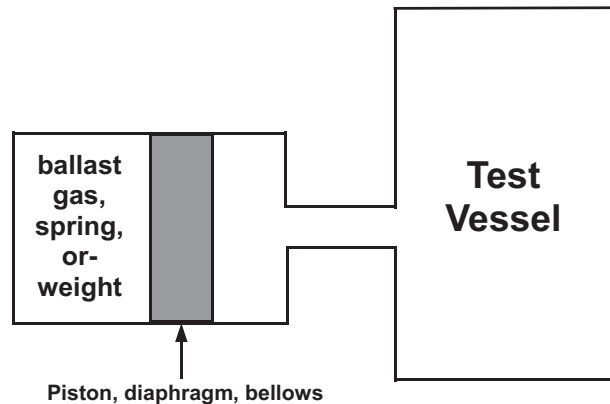


Fig 41—Benefit of a pressure snubber.

suggests a backpressure regulator to clip pressure rise and a forward-pressure regulator can help make up for pressure fall and are also potentially workable.

One can only wonder if mitigation of all these variables would yield more consistent well-behaved results, albeit with a general increase in measured fire limits.

Imagine, if you will, a moment of levity on how a bizarre semicircular specimen, doubtless extremely complex to effect, could be rotated into the combustion zone with a servo system to both measure the flame speed and cut convective issues to a minimum (Figure 42).

Improvement might results, but if not, the bottom line here remains, *G 124-10 is a crashshoot unfit for use.*

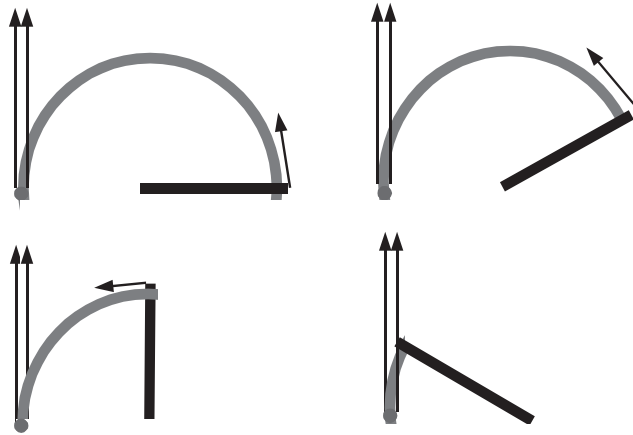


Fig 42—Bizarre extreme approach .

Summary

In 2010 ASTM Committee G4 adopted a short-burn-length criterion to define combustion results as being over the fire limit. Extensive technical arguments to the contrary were not disputed, but were ignored and the integrity of the G4 process was damaged. Instead, the adoption seems apparently based upon intuitive obviousness and the asserted but flawed results of a single test program at the NASA WSTF that concluded 30 mm (1.18 inches) was an adequate burn length criterion to conclude a result is over the fire limit.

The writer has asserted, often, that one needs a burn length criterion large enough to ensure equilibrium combustion or greater was achieved as has been the practice with other forms of fire-limit measurement. The writer has also challenged and disputed the basis for the WSTF work and the otherwise unchallenged conclusion it has drawn.

The writer continues to defend the validity of using a “complete specimen” combustion as a valid indicator of a positive burn in some cases, but he has now stipulated that the use of complete combustion and length criteria that are longer than optimum can unnecessarily protract the test quantity needed.

However, using NASA MSFC data against the background of his own similar earlier testing, he argues that while 3-inch specimens were once considered enormous, and were an enormous leap forward, even they proved to be too short, a problem that 6-inch specimens seemed to have cured. Today we have 12-inch specimen data that may suggest the optimum positive burn length criterion may be somewhere between three and six inches, however, this analysis demonstrates that a 1.18-inch, 30-mm, burn length criterion is way inadequate.

It is intuitively obvious that a metal that burns a lot, in this case 30 mm, might be capable of burning indefinitely,... but this analysis suggests the such intuition *is wrong*. If as reported numerous Companies and the assorted standards on this kind of testing are using a similar short "burn length criterion",....then this analysis suggests *they are wrong*. If as reported, NASA is using the same burn length criterion, then this analysis suggests *NASA is*

wrong. And certainly it suggests the present ASTM Committee G-4 standard *is wrong*.

The consequences of this flaw, are that a less than preferred metal may be chosen for oxygen service. It may then increase the risk for users of that system, and if an incident should result, then it will be difficult to defend the choice in the strict liability environment of a courtroom where the use of "the most compatible of practical materials" is, to the writer's understanding, the most preferred design strategy and defense.

In this analysis the writer has cited, as the writer has been citing for a long time, personal experience and both laboratory and actual fire limit incident results that dispute this change. Furthermore, flaws are cited in the NASA WSTF test program hypothesis that argue not only do the results not support a 30 mm burn-length criterion, but that in fact these results used to defend the adoption of the 30-mm criterion, in fact, prove a 30 mm criterion is much too short.

However, where the combustion of metal rods can be well observed visually or instrumentally, even at elevated pressures, the same tools and criteria used to infer minimum equilibrium combustion in the oxygen index test can be applied to supplement and potentially allow the use of even incomplete combustion results *of almost any size* to define the fire limit.

This analysis is intended to seem brash. But it really is not. The same effects and dilemmas are and always have been present when measuring and interpreting fire limits of gases and liquids and both metallic and nonmetallic and composite solid materials in oxygen index testing at atmospheric pressures.

This not-really-brash assessment is in fact nothing more than a recapitulation of what has been learned and taught to us by the rest of the world's combustion experts outside G-4. G-4 has actually avoided dealing with gas-phase flammability to the writer's great dismay. Some G-4 members have stated a position that gas-phase flammability is not relevant to their mission, because they evaluate oxygen-system hardware, and gases are not structural materials. However, the writer argues they are involved in the combustion of solids, which are just cooled liquids, and they teach crucial lessons on how materials burn.

The writer does hereby clarify and stipulate to an argument that while complete combustion of specimens is perhaps the most valid way to test fire limits including for specimens up to a three- to six-inch length, that it appears it can unnecessarily protract testing at greater criterion length.

Nonetheless, today an expert witness who is testifying, must face the prospect that when an alloy like SS 347 was rejected for use because a crap shoot that allowed its 500 psi threshold to test out as 350 psi, when a less compatible alloy's crapshoot may have allowed its lower threshold to test out higher than 350 psi, then that expert gets to explain why some victim's should not be generously compensated.

Finally some pie-in-the-sky speculation might warrant examination and modest alterations of the G 124 procedure that might just reduce or eliminate some of these known is-

sues with the test and yield more precise and better behaved data.

And on that note this is the finis.

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