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Alan K. Burnham, P. Clark Souers, Franco. J. Gagliardi, Randall K. Weese, Sabrina C. DePiero, Tri Tran, D. Mark Hoffman, Jacob G. Koerner

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What Have We Learned From Decades of CRT, And Where Do We Go From Here?[*]

Alan K. Burnham, P. Clark Souers, Franco J. Gagliardi, Randall K. Weese, Sabrina C. DePiero, Tri Tran, D. Mark Hoffman, and Jacob G. Koerner

[1]Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, CA 94551

The Chemical Reactivity Test, or CRT, has been the workhorse for determining short-to-medium term compatibility and thermal stability for energetic materials since the mid 1960s. The concept behind the CRT is quite simple. 0.25 g of material is heated in a 17 cm^3 vessel for 22 hours at 80, 100, or 120 $^{\circ}$C, and the yield of gaseous products are analyzed by gas chromatography to determine its thermal stability. The instrumentation is shown in Figure 1, and the vessel configuration is shown in Figure 2. For compatibility purposes, two materials, normally 0.25 g of each, are analyzed as a mixture. Recently, data from the past 4 decades have been compiled in an Excel spreadsheet and inspected for reliability and internal consistency. The resulting processed data will be added this year to the LLNL HE Reference Guide. Also recently, we have begun to assess the suitability of the CRT to answer new compatibility issues, especially in view of more modern instrumentation now available commercially.

One issue that needs to be addressed is the definition of thermal stability and compatibility from the CRT. Prokosch and Garcia[1] (and the associated MIL-STD-1751A) state that the criterion for thermal stability is a gas yield of less than 4 cm^3/g for a single material for 22 hours at 120 $^{\circ}$C. The gases from energetic materials of interest ordinarily have an average molecular weight of about 36 g/mol, so this represents decomposition of 0.5-1.0% of the sample. This is a reasonable value, and a relatively unstable energetic material such as PETN has no problem passing. PBX 9404, which yields 1.5 to 2.0 cm^3/g historically, is used as a periodic check standard. This is interesting in itself, since the nitrocellulose in the 9404 is unstable and probably has partially decomposed over the decades. However, it is not clear whether this aging of the standard would lead to more or less gas, since the initial gaseous degradation products are captured by the DPA stabilizer. Clearly this is an issue that needs reconsideration.

The criterion for compatibility is less clearly correct. Although some LLNL reports say that generation of gas in excess of the materials by themselves is an indication of incompatibility, LLNL reports invariably say that materials are compatible if they generate less than 1 cm^3/g of gas. There are two problems with this criterion. First, it is not stated whether the gas yield is per gram of energetic material or mixture. Second, a material that generates >2 cm^3/g by itself could never pass the compatibility tests as stated, because even a mixture of equal masses of that material with a completely inert material would generate >1 cm^3/g of gas per mixture. Furthermore, Prokosch states that a yield equal to or less than from the materials individually means that no reaction has occurred. Clearly, less gas can not be generated unless some type of interaction has occurred. An obvious example would be mixing CaO with a CO_2-generating energetic material. In the absence of any direct action of the CaO on the energetic material, the CO_2 product would be captured by the CaO, thereby decreasing the gas yield and liberating considerable heat. In a large, closed volume, this could tip the balance to thermal runaway.

Those testing materials for compatibility should consider the nature of the chemicals being mixed to be sure that this type of situation cannot occur.

Consequently, even though the criterion of <1 cm³/g of mixture is normally a good test for materials which are quite thermally stable by themselves, it can cause either false negatives or false positives in some situations. This has led us to revisit both the compatibility criterion and measurement method, which will be taken up later in this paper. In the meanwhile, we use a provisional new criterion of <1 cm³ of incremental gas per gram of mixture as a compatibility limit. It should be kept in mind that a total gas yield of <4 cm³/g of mixture should also be satisfied, because it would take a smaller amount of incremental decomposition to cause a thermal runaway with a thermally labile energetic material than with a thermally refractory energetic material.

Most materials investigated in the CRT, both energetics and materials they will come in contact with (called "aliens" in this paper and the data base), are expected, by experience, to pass both the thermal stability and compatibility criteria. Gas yields and standard deviations at 120 °C for common explosives are summarized in Table 1. Materials tested over the years for use with energetic materials can be grouped in various classifications. Gas yields from these materials are also shown in Table 1.

While the most rigorous compatibility testing would measure the gas yields from the precise materials (energetic and alien) to be used in a particular situation, it is acceptable to use prior measurements on the individual materials to establish a baseline. On the other hand, if the intrinsic gas generation of two materials is thought to be low, it is acceptable, and in fact more restrictive, to test only the mixture and to revert to the simpler criterion of <1 cm³/g of mixture. Another approximation would be to subtract the average gas generation value for the class of alien material listed in Table 1. However, all but the foam materials are relatively close in their gas generation values, so, in the version of the data base to be posted, the excess gas generation for mixtures of energetic materials with alien materials (except foams) is calculated using an average value for all non-foam aliens: 0.2 cm³/g.

Summary listings of the compatibility of various energetic materials with other materials are given in the current HE Reference Guide. As part of the current updating of the CRT data base, we are cross-checking those summaries against CRT data. Minor discrepancies are being addressed.

One potential weakness in the current CRT system is that the gas yields are determined by integrating the yields of N_2, O_2, Ar, CO, NO, N_2O and C_2O. The GC sample loop is at the manifold pressure, and the amount of gas injected is proportional to the gas in the reactor vessel. Ar and O_2, of course, are indicative of air leaks in the system rather than thermal decomposition. While this suite of gases undoubtedly captures most of the species from energetic materials, it does not necessarily capture all the species from decomposition of the alien materials. Furthermore, an error in the calibration or identification of any species is reflected in the total gas yield. Consequently, a new manifold and gas analyzer have been constructed. In this case, the gas yield will be measured directly by a pressure transducer, and the composition will be measured by both thermal conductivity and mass spectrometric detectors. The determination of compatibility does not depend directly on the gas composition. However, the new system will be able to determine not only whether air leaks have contaminated the sample but also whether there are additional gases present that can reveal the nature of the chemical reactions causing the incompatibility.

An additional issue is whether CRT is the correct method to detect compatibility with two-part epoxies. The first question is whether the epoxy will be placed in contact with the energetic material in the curing or cured state in the application of interest. The latter case is analogous to compatibility testing for other materials, but compatibility during curing is another matter. In a complete investigation, one might want to run a CRT with each component of the epoxy mixed separately with the energetic material. However, that does not seem warranted

normally. Instead, we have added a preliminary step in which visual observation of a curing mixture of epoxy and powered energetic material (color changes and bubble formation) determines whether the epoxy is safe to apply in thin layers. Depending on the knowledge of the materials and the likelihood of compatibility, the observation can be made first on the mg scale. The CRT samples can be mixed and observed in the same manner before being placed in the reactor for thermal assessment after curing. In this case, the CRT is appropriate for answering two questions. If the sample is heated after curing, it is most relevant to assessing compatibility for storage of an assembly from days to months. Heating of the uncured mixture is not ordinarily warranted unless the epoxy is to be applied in thick layers that will undergo self-heating during curing.

A further improvement planned next year is the activation of a heat flow calorimeter having gas pressure monitoring capability that was recently purchased. The sensitivity of this calorimeter, from Thermal Hazard Technology, is about 0.5 µW. For comparison, an energetic material with a heat content of 5000 J/g generates a power of 60 µW/g if 0.1% of its energy is released over a day. This heat should be easily detected. In practice, thermal stability or compatibility would be measured by heating the material or mixture to 120 ^{o}C by some thermal program yet to be determined, and heat flow (endothermic or exothermic) and gas generation from the sample would be monitored continuously. This proposed method provides two independent measures of reactivity. At the end of the experiment, the sample vial can be analyzed for gas composition, if desired.

1. D. W. Prokosch and F. Garcia, "Chemical Reactivity Test for Thermal Stability," in 26th Department of Defense Explosives Safety Seminar, Miami, FL (Aug. 1994).

Table 1. Summary of gas generated from selected energetic and alien materials over the past four decades in the LLNL CRT for 22 h at 120 ^{o}C.

| Energetic Material	Avg. cm^3/g	Std. Dev.	Alien Material	Avg. cm^3/g	Std. Dev.
CL-20	0.18	0.15	Plastics	0.07	0.07
HMX	0.12	0.06	Silicon potting	0.08	0.08
LLM-105	0.03	0.03	Metals	0.08	0.10
PETN	0.59	0.30	Lubricants	0.12	0.10
RDX	0.18	0.12	Inorganics	0.12	0.18
TATB	0.11	0.09	Wrapping materials	0.16	0.11
TNT	0.08	0.15	Colorizers/ Taggants	0.16	0.16
LX-04	0.08	0.05	Sealants	0.22	0.25
LX-09	0.17	0.05	General tapes	0.22	0.22
LX-10	0.10	0.07	Complicated mixes	0.25	0.29
LX-14	0.11	0.06	Rubbers	0.26	0.22
LX-17	0.19	0.17	Adhesives	0.30	0.26
LX-19	0.61	0.32	Organics	0.33	0.25
XTX-8004	0.13	0.12	**All above**	**0.19**	**0.22**
PBX 9404	1.61	0.35			
PBX 9407	0.14	0.05	Foams	0.81	0.64
PBX 9501	0.25	0.23			
PBX 9502	0.18	0.14			
Black powder	0.26	0.07			
C4	0.19	0.11			
Comp B	0.25	0.11			

Figure 1. Photograph of the current LLNL CRT system.
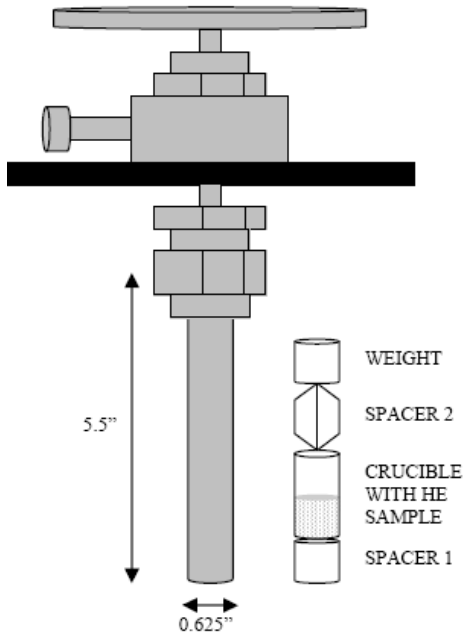
Figure 2. Reactor vessel of the LLNL CRT.