



U.S. Department
of Transportation

Pipeline and Hazardous Materials
Safety Administration

1200 New Jersey Ave., SE
Washington, DC 20590

NOV 19 2008

Mr. Kevin Greene
Hazardous Materials Distribution Consultant
DuPont Global Logistics
12650 Highway 43 North
Axis, AL 36505

Ref. No. 08-0214

Dear Mr. Greene:

This responds to your letter dated August 22, 2008 regarding classification of Division 4.2 self heating substances under the Hazardous Materials Regulations (HMR; 49 Parts 171-180). Specifically you asked for our concurrence concerning the technical merit of an alternative to the testing method described in the UN Manual of Tests and Criteria, 4th revised edition (UN Manual). The specific requirements you address are contained in section 33.3 of the UN Manual and are implemented through the provisions of § 173.124 of the HMR.

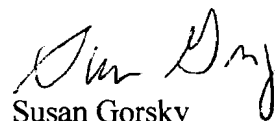
The UN Manual describes a Division 4.2 self-heating material as a material that, when in contact with air and without an energy supply, is liable to self-heat. A material of this type exhibits spontaneous ignition or experiences dangerous self heating described by a 60 °C rise in temperature over the oven temperature within 24 hours. The UN Manual specifies that substances with a temperature of spontaneous combustion higher than 50 °C for a volume of 27 m³ should not be assigned to Division 4.2.

The method described in the UN Manual requires testing of samples in 25 mm and 100 mm cubes at discrete temperatures to establish whether a material meets the definition of a Division 4.2 self heating material and to determine the packing group. Your alternative method utilizes a simplified self heating-model based on Frank-Kamenetskii ignition theory to extrapolate from experimentally obtained, small scale data the spontaneous ignition temperature of a given substance at a 27 m³ mass.

We have reviewed the information provided with your letter and we agree that the alternative test method you propose will accurately establish the self-ignition temperature of a solid material of a given mass consistent with the guidance provided in the UN Manual.

I hope this satisfies your inquiry. If we can be of further assistance, please contact us.

Sincerely,

A handwritten signature in black ink, appearing to read "Susan Gorsky". The signature is fluid and cursive, with the first name "Susan" and last name "Gorsky" clearly distinguishable.

Susan Gorsky
Acting Chief, Standards Development
Office of Hazardous Materials Standards

Leary
§173.124(b)(2)
Classification
08-0214

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August 22, 2008

Mr. Edward T. Mazzullo
Director, Office of Hazardous Materials Standards
U.S. DOT/PHMSA (PHH-10)
1200 New Jersey Avenue, SE East Bldg., 2nd Floor
Washington, DC 20590-0001

Dear Mr. Mazzullo:

Subject: Request concurrence that extrapolated small-scale data may be used to establish whether a solid material should be classified as a Division 4.2 self-heating substance, defined as having a critical temperature of 50° C or less for a 27 m³ cubic mass.

Statement of Issue

49 CFR 173.124(b)(2) specifies that criteria found in Test Method N.4, Section 33.3.1.6 of the *United Nations Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*, 4th revised edition, be used to determine whether a solid-phase substance should be classified as a Division 4.2 self-heating hazard. However, this test method may not always result in a correct classification. It is suggested that in many such situations the application of self-ignition theory coupled with isothermal oven tests may be more appropriate to classify a substance as self-heating, which in the context of the *UN Recommendations* means that a test substance exhibits a self-ignition temperature of 50° C or less for a 27 m³ mass.

Discussion

Background

Many organic solids will oxidize when exposed to air. For a given mass the heat generated from these exothermic reactions at low temperatures will most likely be safely dissipated to the environment and very little if any increase in material temperature will occur. However, as the air temperature surrounding the material increases the oxidation reaction rate and attendant rate of heat generation also increase until a point is reached where all the heat generated cannot be dissipated and material temperature will begin to equilibrate above that of the surrounding air. As the surrounding air temperature is raised further the oxidation rate will continue to rise until a condition is reached where heat accumulated in the solids reaches a 'point of no return' and the sample exotherms to its ignition point. This temperature, referred to as the *critical temperature* (T_c), is highly dependent upon reaction kinetics, physical and thermal characteristics of the solid, and surface area-to-volume ratio and geometry of the mass. Larger material masses of a given geometry will exhibit lower critical temperatures since they are

less able to dissipate heat due to their lower surface area/volume ratio. For the same reason different geometries of a given mass of material will show different critical temperatures. It is therefore impossible to speak of a single 'critical temperature' for a given material since this value will be situation-specific. A simplified self-heating model based on Frank-Kamenetskii ignition theory was developed by Gray and Lee¹ and further refined by Bowes² to deal with this problem and has been widely applied to the evaluation of self-heating hazards in industry. This model assumes that one chemical reaction is responsible for self-heating over the temperature range of interest and that the solids temperature rise above the surrounding air temperature is small in comparison to the ratio of activation energy to the universal gas constant. It is also assumed that rate of heat loss is governed by heat conduction through the solids as opposed to convective heat transfer rate at the surface (i.e., Biot number >30). A good abbreviated description of this method is given by Gray³ and Grossel and Zaolsh⁴. Based on this model boundary conditions for criticality are defined by the equation:

$$\ln(\delta_c T_c^2 / r^2) = M + (N/T_c) \quad (\text{Equation 1})$$

where:

δ_c = Geometry Dependent Constant (2.52 for cube)
 T_c = Absolute Critical Temperature for Exothermic Runaway
 r_c = Characteristic Length (half-length of a side for a cube)

Parameters M and N are defined as:

$$M = \ln(E_A Q \rho A / Rk)$$

$$N = E_A / R$$

Where:

E_A = Activation Energy
 Q = Heat of Reaction
 ρ = Solids Bulk Density
 A = Pre-exponential factor in the Arrhenius reaction rate equation
 R = Universal Gas Constant
 k = Solids Thermal Conductivity

Practical application of the model involves first conducting isothermal tests in a forced convection oven to determine critical temperature for material housed in open mesh containers of a given geometry (e.g., cubes fabricated from screen) at different volumes. The experimentally determined critical temperatures are then used to construct a plot of reciprocal absolute temperature ($1/T_c$) vs. $\ln(\delta_c T_c^2 / r^2)$. A linear regression on these data yields a line of slope N and intercept M . These values may then be used with Equation 1 to determine the critical temperature for other volumes and geometries, or alternatively the critical volume for different geometries at a given critical temperature.

Relevance to United Nations Test Method N.4

Test Method N.4 as described in the *UN Recommendations*⁵ requires testing of samples in 25 and 100 mm cubes at discrete temperatures to establish whether a substance must be classified as a Division 4.2 self-heating hazard and if so to determine the appropriate packing group. Tests are based on the self-heating behavior of charcoal, which has a critical temperature of 50° C for a 27 m³ cubic mass. Charcoal has been found to follow the simplified self-heating model described in the previous section (figure 1). Since tests on 27 m³ masses are impractical another point on the self-heating curve, 140° C at a 1000 cm³ cubic volume, was selected as an 'equivalent' test. If an initial test on a test substance at this condition proves positive, defined as a temperature rise of >60° C at the center of the mass for a 24-hour test period, the self-heating behavior of the sample is determined to be equivalent to or worse than that of charcoal and the material is classified as Division 4.2. This decision is based on the assumption that the self-heating behavior of the test substance is similar to that of charcoal, which may not always be the case. Figure 2 shows a situation in which a substance which failed the

initial test at 140° C in the 1000 cm³ cube was tested in cubes of various sizes to establish a self-heating curve. For this case all of the assumptions of the simplified self-heating model were satisfied and an extrapolated self-ignition temperature of 57.8° C was determined for a 27 m³ cubic mass. The difference in the thermal response of the test material from the behavior of charcoal is explained by the much higher activation energy of the test substance as shown by the higher value of the self-heating curve slope, which is the ratio of activation energy to universal gas constant (parameter N in Equation 1 above). Based on this analysis the substance should not be classified as Division 4.2 per Section 33.3.1.3.3 of the UN Recommendations which states that:

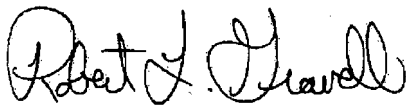
"...Substances with a temperature of spontaneous combustion higher than 50° C for a volume of 27m³ should not be assigned to Division 4.2."

A recent seminar on the UN self-heating protocol presented at the International Group of Experts on the Explosion Risks of Unstable Substances (IGUS)⁶ reached conclusions essentially identical to those discussed in this document.

Proposal

It is proposed that extrapolated small-scale data may be used to establish whether a solid material should be classified as a Division 4.2 self-heating substance, defined as having a critical temperature of 50° C or less for a 27 m³ cubic mass. This method is limited to conditions for which the assumptions in the simplified Frank-Kamanetskii self-heating model are valid. We would appreciate PHMSA/DOT's concurrence in the technical merit of our approach to Division 4.2 classification and our position that this method is consistent with guidance provided in the UN Recommendations.

Please direct technical questions regarding this document to Robert L. Gravell and direct PHMSA/DOT's final response to Kevin M. Greene at the address provided.



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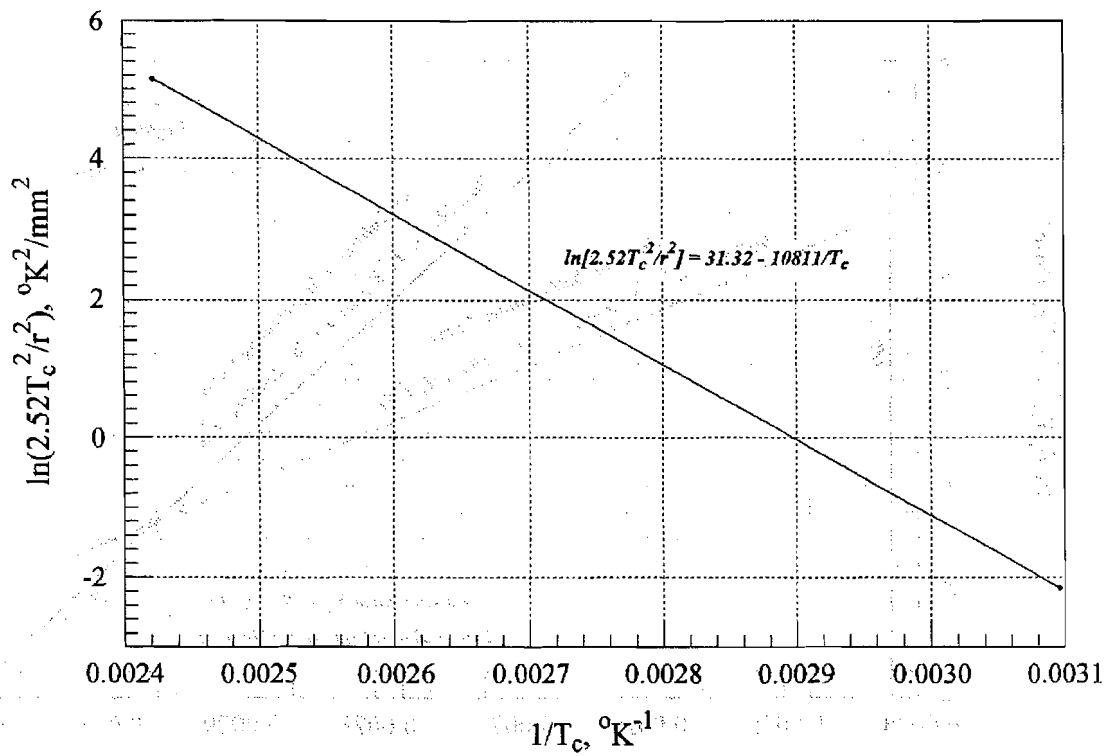
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1. *Oxidation and Combustion Review*, Vol. 2, P. Gray and P. Lee, Elsevier, 1967
2. Bowes, P.C., *Self-Heating: Evaluating and Controlling the Hazards*, Elsevier Press, Oxford, 1984
3. *SFPE Handbook of Fire Protection Engineering*, 3rd edition, NFPA, Quincy, 2002
4. Grossel, S.S and Zalosh, R.G., *Guidelines for Safe Handling of Powders and Bulk Solids*, AIChE Press, New York, 2005
5. *Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*, 4th revised edition, United Nations, 2003
6. Wildner, W., "Anomalous Self-Heating Behavior: A Serious Gap in the Regulations," IGUS-EOS Meeting, May 2008

Figure 1

Charcoal Self-Heating Curve per UN Recommendations



Note: Based on critical temperatures of 140° C and 50° C for cubes 0.1 and 1.5 m on a side, respectively

Figure 2

Critical Ignition Data for Test Substance vs. Charcoal

