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THERMAL STABILITY AND COMPATIBILITY PREDICTIONS

FOR THE EXPLOSIVE EAK

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ABSTRACT

EAK [mixtures of ethylenediamine dinitrate (EDD), ammonium nitrate (AN), and potassium nitrate (KN)] is a castable high explosive. Within the temperature range necessary for casting, there will always be a size and shape that will self-heat to explosion. Current predictive models for critical temperature of EAK systems are reported, and effects of admixture with aluminum and rust are discussed.

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INTRODUCTION

All explosives decompose chemically with an evolution of heat. The laws of chemical kinetics predict that decomposition will proceed at some rate at all temperatures, and decomposition is more rapid in a liquid phase than in a crystalline solid phase. Safe formulation, fabrication, and application of any explosive require an ability to predict the explosive's response to heating in any size and shape.

EAK shows a solidus temperature at 103.6°C (1), and it will show a finite decomposition rate whenever a liquid phase is present. No predictive model has previously been reported for the self-heating hazards of EAK, and we have not been able to obtain complete records or reports of previous applications of similar systems. It is known that a mixture of AN and EDD was used in Germany (2), but the scale of the operation is not known.

A 227-kg melt is the largest that has been reported to us. The kettle was approximately 73 cm in diameter, and the melted charge was approximately 46 cm deep. The maximum temperature reached was 110°C. The fact that the kettle did not explode does not prove that the critical temperature for that size and shape

was above 110°C, because the time to explosion at that temperature can be greater than the operational time. However, the safety of the melt must be explained by any predictive model.

The response of an explosives system to heating is determined by the balance between the rate heat is produced by the chemical decomposition of the system and the rate heat is dissipated by physical processes. With highly energetic materials, thermal hazards can be predicted under two limiting conditions: (1) heat flow from the reacting mass by conduction only, with establishment of a thermal gradient, and (2) heat flow by convection only, with the thermal gradient at the boundary. Approach to the second condition in practice requires vigorous stirring, and it will always result in a significantly higher limiting temperature for safe operations. Efficient stirring and efficient heat transfer at the boundary greatly improve safety.

Hazards under conditions of pure conduction can be predicted by use of the Frank-Kamenetskii equation (3).

$$\frac{E}{T_C} = R \ln \frac{a^2 \rho Q Z E}{T_C^2 \delta \lambda R} \quad (1)$$

where T_C is the critical temperature, E and Z are the

activation energy and pre-exponential from the Arrhenius equation, a is a dimension (for example, radius of a sphere or infinite cylinder or half thickness of an infinite slab), ρ is the density, Q is the heat of the self-heating reaction (not heat of detonation or combustion), R is the gas constant, λ is the thermal conductivity, and δ is a shape factor (3.32 for spheres, 2.0 for infinite cylinders, 0.88 for infinite slabs, and approximately 2.7-2.8 for cylinders with length = diameter).

The critical temperature is defined as the lowest constant surface temperature for a specific size and shape of a specific composition at which the system can self heat catastrophically.

The material will still decompose below the critical temperature, and confined systems will ultimately rupture as a result of pressure increase; however, the system will not self-heat to explosion or detonation at temperatures below the critical temperature.

A specific size and shape of explosive will ultimately self heat to ignition, explosion, or detonation at temperatures above T_c , but the time to explosion depends on the characteristics of the specific system. Times to explosion can be quite long at temperatures near the critical temperature. It can be safe to

operate at temperatures above T_C when times to explosion are known to be sufficiently long, but a sufficiently high T_C eliminates worries about time to explosion.

Hazards under conditions of pure convection can be predicted with the Semenov model (4),

$$VQ\rho Ze^{-E/RT_C} = \alpha SRT_C^2/E \quad (2)$$

where T_C is the critical temperature, V is the volume of the charge, Q is the heat of reaction, ρ is the density, E and Z are the activation energy and pre-exponential, S is the surface area of the charge, R is the gas constant, and α is the heat-flow coefficient at the boundary.

Our normal procedure for producing thermal-hazards predictive models is to measure the physical properties of a material, measure the critical temperature of a known size and shape of the material (5), measure E and Z with isothermal runs at different temperatures in a differential scanning calorimeter (DSC), and test the T_C predictions made from the models against the experimental measurement. When the predicted value of T_C agrees with the experimental value, we feel that predictions for other sizes and shapes can be made with

some confidence. Greater confidence is achieved by additional testing at larger sizes (6), a procedure that is facilitated by the existence of a predictive model.

Limited financial support for the program and the complexity of the EAK system have made it impossible for us to pursue our normal approach in establishing predictive models. The reported procedure is intended to be an illustration of how data from different sources can be combined to provide useful models at moderate cost in time and money.

Predictive models at the stage of development reported here must never be used for predicting the safety of production-scale operations. These models are intended for use only during the development phases of the EAK program.

EXPERIMENTAL

Isothermal rate measurements were made with a Perkin-Elmer DSC-1B differential scanning calorimeter. Samples were encapsulated in aluminum cells,

Perkin-Elmer Part Number 219-0062, and the cells were perforated with a single hole approximately 0.15 mm in diameter. The internal free volume of the cells was reduced as much as possible by sealing aluminum discs into the cells with the samples.

The time-to-explosion test for the determination of experimental critical temperatures (5) uses empty aluminum blasting-cap shells, DuPont E-83 (approximately 6.5-mm ID by 4-cm long, weighing approximately 0.72 g empty). A 40-mg sample of the explosive (exclusive of additives) is pressed into the shell under a hollow aluminum plug, the skirt of the plug is flared to maintain constant geometry during heating, and the sample thickness is measured as accurately as possible. The assembly is lowered into a preheated metal bath, and the time to explosion is measured. The lowest temperature at which an explosion can be obtained is the critical temperature, T_c .

Reynold's H-5 aluminum was used for all of the compatibility tests, and the rust was scraped from weathered structural-steel angle iron. The EDD was prepared by neutralizing ethylenediamine with nitric acid in an ethanol medium, and the EAK used was a 45.7/46.2/8.1-EDD/AN/KN mixture. The EAK sample chosen

gave the highest T_C in our test of any available sample (248°C as a 0.08-cm-thick disc).

RESULTS AND DISCUSSION

When nothing but an experimental T_C is known for a specific size and shape of a material, tentative (worst-case) predictive models can be made from the Frank-Kamenetskii equation. In order to do this, the real dimensions, shape, and density used in the T_C measure are substituted into the F-K equation (1), guesses are made for E , and corresponding values for the "inner product,"

$$\frac{\rho QZE}{R \lambda} \quad (3)$$

are calculated. Individual values for Q , Z , R , λ , and ρ need not be known, because their product is a constant for any specific material. The result can then be used to predict T_C for other sizes and shapes of the same material. T_C estimates are not very sensitive to density differences.

In order to make earliest estimates of safety limits for EAK on the basis of the measured T_C , we had to set reasonable limits for E . It is highly unlikely that EAK will be found to be more stable than pure AN, and the highest value for the E of AN that can be found in the literature is 49.45 kcal/mole (7). The lowest value for any EAK component that could be found was a value of 34 kcal/mole for EDD (8). Since mixtures

often show lower activation energies than either component, we could not guarantee that the worst-case predictive model for EAK involved an E of 34 kcal/mole. A measured E is always a great help in estimating safety limits.

Figure 1 shows worst-case predictions of T_c versus size that are based on the F-K equation (1) and assumptions that $E = 30$ kcal/mole or $E = 50$ kcal/mole. The 30 kcal/mole value seems unlikely, because it predicts a T_c well below the temperature used for the 227-kg melt. Figure 1 shows the importance of obtaining the most accurate values for E possible.

Unfortunately, it is not always obvious what constitutes an "accurate" activation energy for an explosive. It is important that the kinetics constants used in a self-heating predictive model be those that correlate with the chemical process responsible for catastrophic self heating. Unless a complex process can be separated into its component reactions and the constants for each component reaction can be measured, the required correlation cannot be made with confidence. The decomposition of EAK is exceedingly complex, and it has not been possible as yet to separate the process into its component reactions.

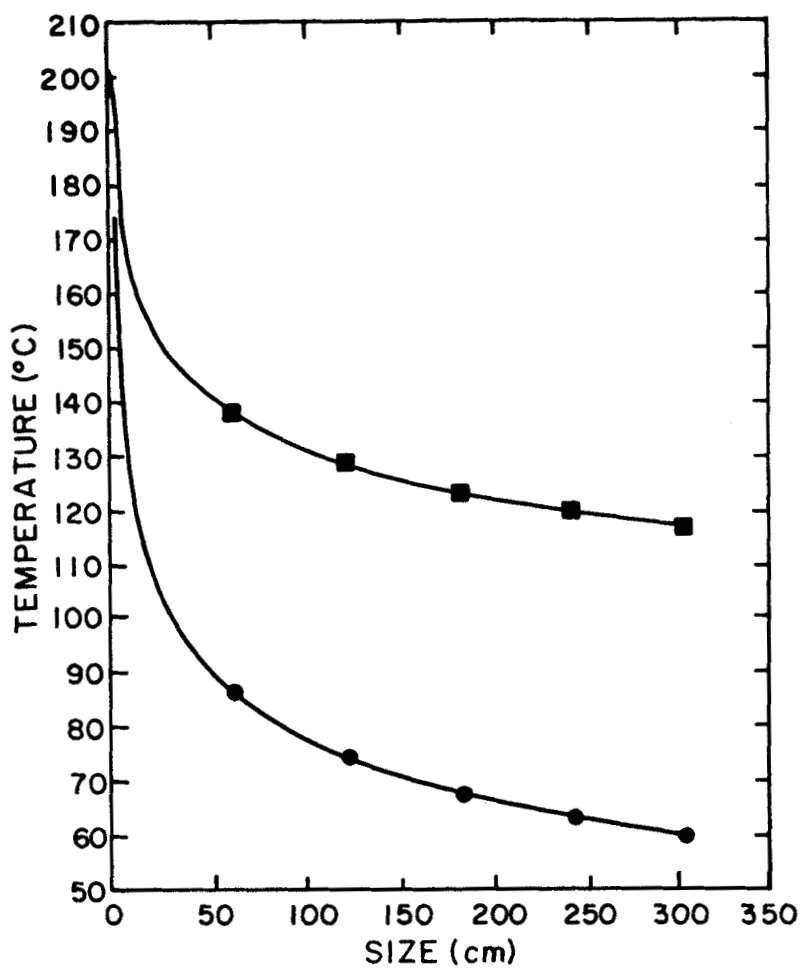


Figure 1. Critical-temperature predictions for EAK in cylindrical geometry, normalized to the experimental T_c . The upper curve assumes $E = 50 \text{ Kcal/mole}^{-1}$; the lower curve assumes $E = 30 \text{ Kcal/mole}^{-1}$.

Figure 2 shows the only three accurately comparable rate curves we have been able to obtain for EAK. They show a significant, temperature-dependent initial-rate process, an obvious induction time, a very sharp major decomposition, and a very sharp final process. Observations made during development of the method showed that time to maximum rate was changed significantly by changes in both sample size and the free volume of the DSC cell, making it exceedingly difficult to obtain reproducible results. Precision was improved by close control of experimental conditions. Very small samples (0.5 mg) were required to reduce the tendency to self-heat catastrophically during the acceleratory phase of the decomposition. In order to control frothing, the samples were fused into the cells under the aluminum discs at a temperature only slightly above the melting temperature of EAK. The samples were checked for weight loss as a result of fusion, and no weight loss was detected.

It is important to recognize the fact that thermal hazards of EAK are system dependent. We cannot currently predict the dependence, but we believe that confinement improves safety.

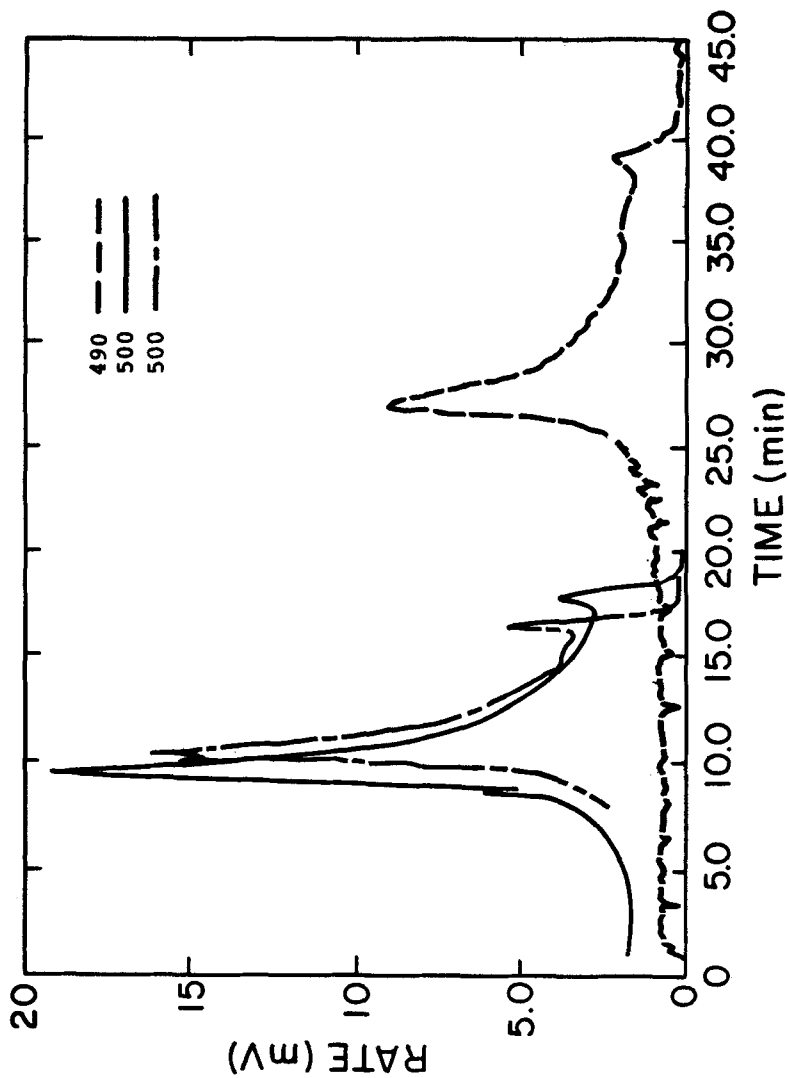


Figure 2. Isothermal DSC rate curves for EAK. The two curves that are nearly superimposed were made at 500 K; the single curve was made at 490 K.

When a rate process follows a normal rate law $dx/dt = k(1 - x)^n$, where x is the fraction decomposed, k is the chemical rate constant, and n is the reaction order, a plot of the rate data as shown in Figure 3 will give a straight line with a positive slope of n . Figure 3 proves that no part of the EAK decomposition follows a normal rate law.

Figure 4 shows the rate data plotted according to an autocatalytic rate law. The acceleratory process is autocatalytic; however, the autocatalytic process does not have a significant temperature effect ($E = 0$). Evaluation of the induction reaction gives an extremely high value for E that cannot be justified. The only logical basis for evaluation of the data involves measurement of the time to the maximum rate. The temperature coefficient of the rate that is obtained from an Arrhenius plot of times to maximum rate is 47 kcal/mole. We currently consider this to be our "best value" for use in predictive models, and it appears to provide a consistent set of predictions for all existing heating tests.

When the induction-time-based E (47 kcal/mole) is used in the F-K predictive model that is obtained from the experimental T_c , the predicted critical temperatures in Figure 5 are obtained.

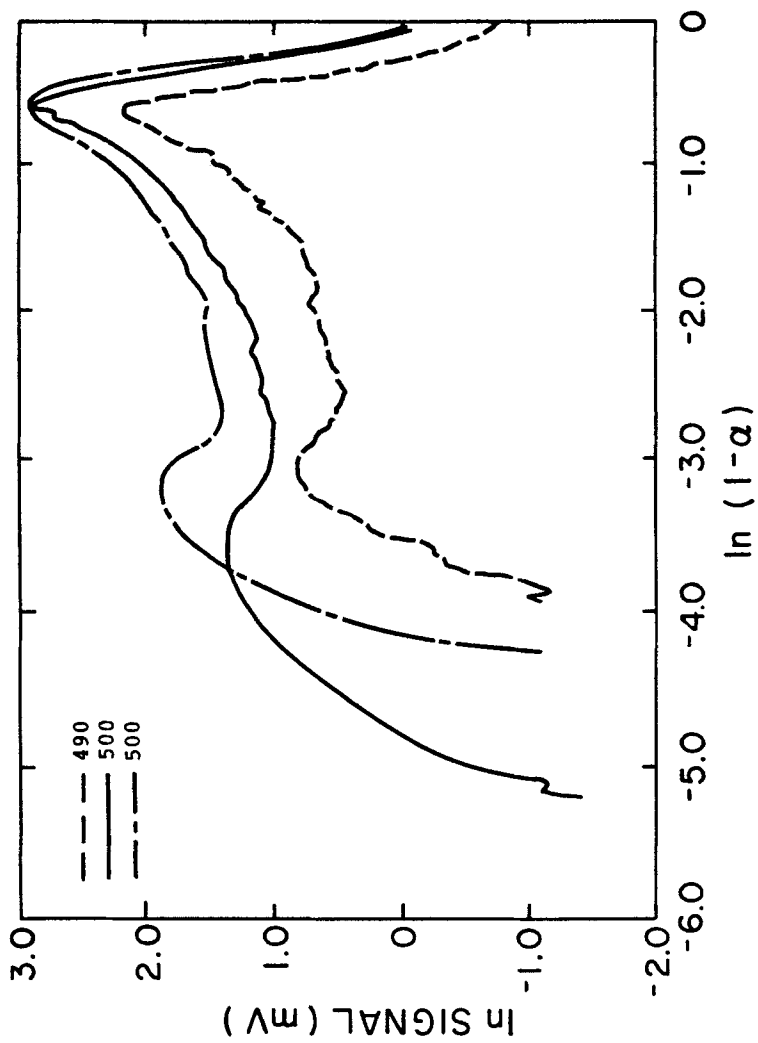


Figure 3. Order plots of EAK rate data from Figure 2. The absence of straight-line segments with positive slopes shows that there are no simple component reactions in the complex decomposition process.

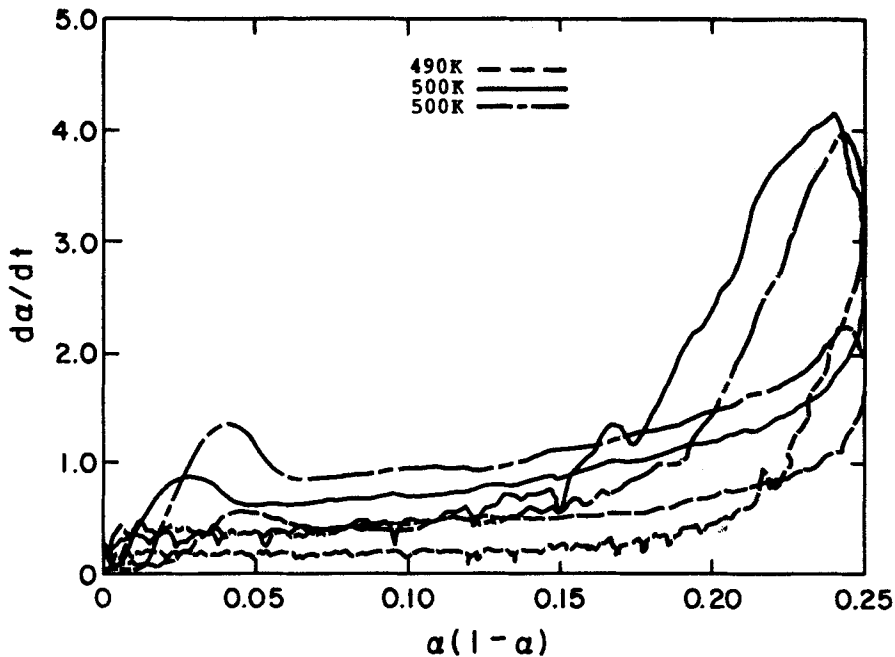


Figure 4. EAK rate data from Figure 2 plotted according to a simple $[d\alpha/dt = k\alpha(1-\alpha)]$ autocatalytic rate law. The early part of the process shows a temperature-dependent initial rate and a long, nearly horizontal straight-line segment. The acceleratory phase of the process produces the steep, straight-line segment near the right margin, but the slope of that segment does not appear to change significantly with temperature ($\Delta E \approx 0$). The small hump near the left margin is caused by the final sharp phase of the decomposition (Figure 2). This type of rate-law plot reflects back on itself at $\alpha = 0.5$ (where $\alpha(1-\alpha) = 0.25$)

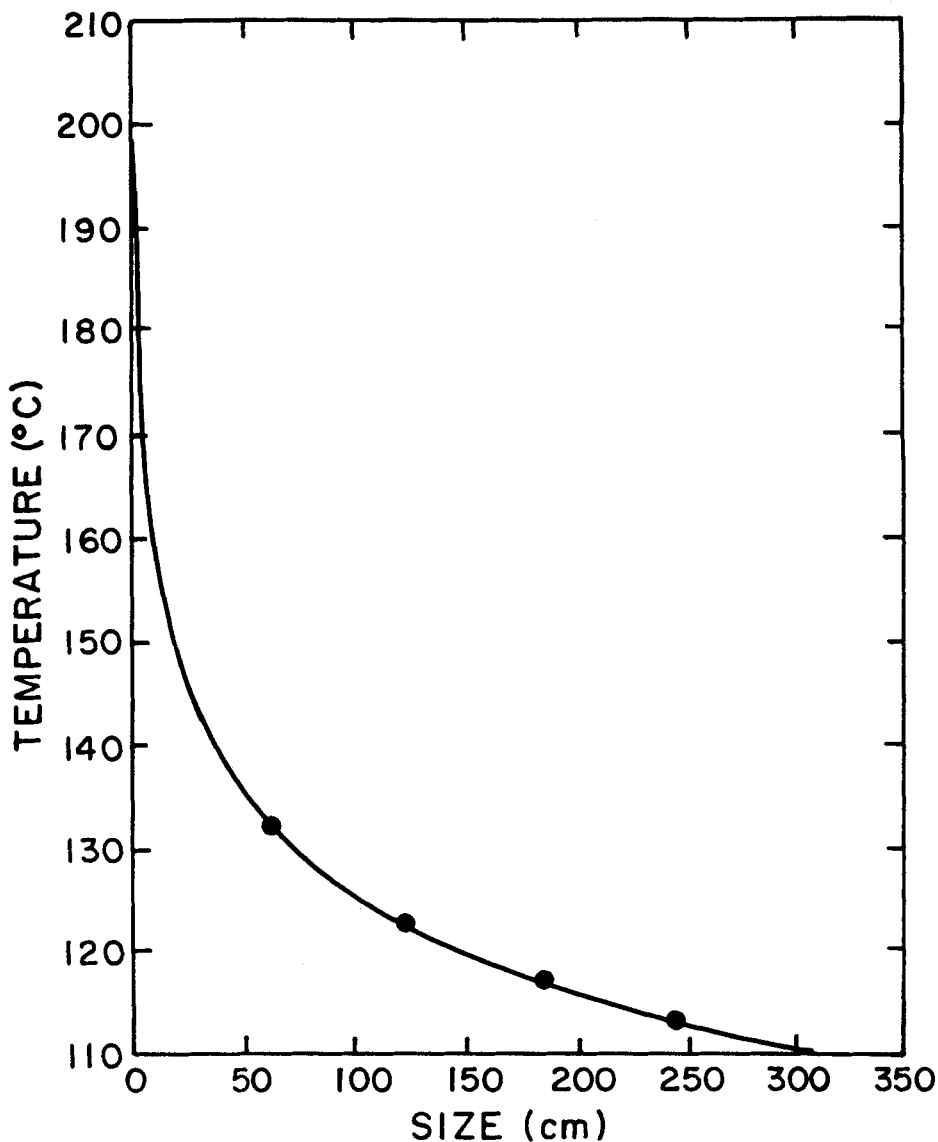


Figure 5. Critical temperature versus size (diameter of casting kettle) predictions for pure EAK according to a Frank-Kamenetskii (worse-case) model with $E=47$ Kcal/mole, normalized to the experimental measurement. The model assumes no convective cooling or stirring.

When some of the values in the "inner product" (equation 3) are available, it is possible to make a rough test of the credibility of the predictive model that is based only on a measured T_c and a guessed E . In the case of EAK, Q has been measured in a moderately confined system with the Accelerating-Rate Calorimeter (ARC) as approximately 450 cal/g. High explosives usually give values between about 300 and 750 cal/g for the self-heating process, and the model is not especially sensitive to Q . We can assume a slightly higher Q than measured for a more completely confined system without being unrealistically conservative. R is known ($1.987 \text{ cal K}^{-1} \text{ mole}^{-1}$), and most explosives have thermal conductivities on the order of $5 \times 10^{-4} \text{ cal cm}^{-1} \text{ s}^{-1} \text{ K}^{-1}$. The density of liquid EAK at 110°C was determined to be 1.46 g cm^{-3} , but the model is not very sensitive to density.

The measured T_c for an 0.08-cm-thick slab of our best sample of EAK is 521 K (248°C). Assuming that E is $47000 \text{ cal mole}^{-1}$, the calculated inner product is 8.72×10^{27} . Substituting the indicated values for everything but Z , the calculated Z is found to be $2.22 \times 10^{17} \text{ s}^{-1}$. Keenan and Dimitriadis (7) reported a Z of $3 \times 10^{16} \text{ s}^{-1}$ for pure AN; therefore, our

calculated value for the EAK mixture does not seem unreasonable.

The values used in the model that generates Figure 5 are the following: $\rho = 1.46 \text{ g cm}^{-3}$, $Q = 500 \text{ cal g}^{-1}$, $Z = 2.22 \times 10^{17} \text{ s}^{-1}$, $E = 47000 \text{ cal mole}^{-1}$, $\delta = 2.72$ (for a right-circular cylinder with $l = d$), and $\lambda = 5 \times 10^{-4} \text{ cal s}^{-1} \text{ cm}^{-1} \text{ K}^{-1}$. When $a = 0.04 \text{ cm}$ and $\delta = 0.88$ (our time-to-explosion test approximates slab geometry), the model reproduces the measure T_C of 521 K.

We realize that the Frank-Kamenetskii model requires heat-flow conditions that are unlikely in a real melt kettle, because natural convection will always be observed in a fluid system. However, that model should provide a reasonable worst-case limit for operations in a melt kettle. If the model predicts a T_C that is well above expected operational temperatures for any size and shape, the operation should be safe from the thermal-hazards standpoint. For example, we were requested to predict the safety of a 50-gal (80-cm-diameter) melt at 110°C. The T_C predicted from Figure 5 is 129°C; therefore, use of the kettle should be safe. Stirring and/or natural convection will improve the safety margin.

Some indication of the safety margin to be expected as a result of stirring or natural convection can be obtained from a very simple application of a Semenov model (4); however, predictions made according to a Semenov model are sensitive to the value chosen for the heat-transfer coefficient (α). Dubovitskii, et al., reported values ranging from 0.0105 to 0.0135 cal cm⁻² s⁻¹ K⁻¹ for thin glass walls in flowing glycerol (9), and values on the order of 0.018 cal cm⁻² s⁻¹ K⁻¹ have been reported for fluid-jacketed melt kettles (10). A value of about 1.5×10^{-3} cal cm⁻² s⁻¹ K⁻¹ may be appropriate for steam-jacketed kettles (10). When we normalize our experimental T_c against a Semenov model, we obtain a calculated α of 8.5×10^{-3} cal cm⁻² s⁻¹ K⁻¹ for our time-to-explosion test, which does not seem unrealistic.

If we assume the calculated α , the predicted values marked "Semenov, Al Wall" in Figure 6 are obtained. Since the thermal conductivity of steel is only about 26 percent of that for Al, we can assume that α for a steel vessel would be about 0.0022 cal cm⁻² s⁻¹ K⁻¹. The curve in Figure 6 marked "Semenov, Fe Wall" is obtained from the Semenov equation (2) and the lower value for α .

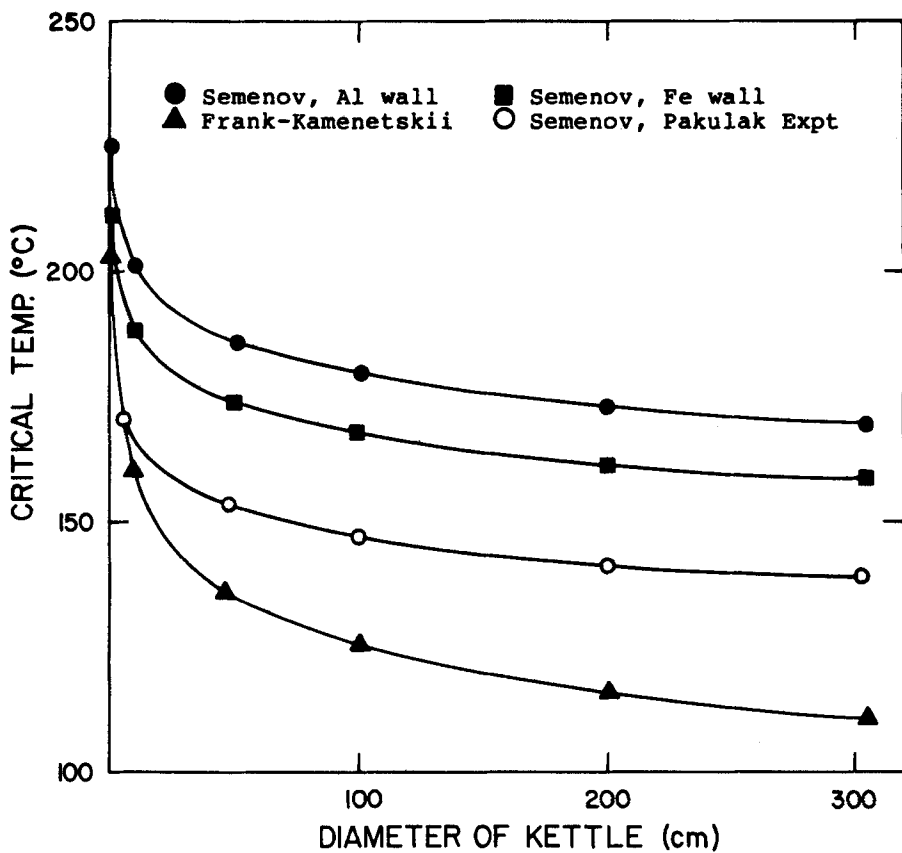


Figure 6. Critical-temperature predictive models for pure EAK.

As can be seen from Figure 6, our lowest "realistic" Semenov T_C prediction for a 10-foot-diameter stirred kettle is 158.5°C. This would indicate that all normal operations with pure EAK should be safe from the standpoint of thermal hazards; however, the models used to produce Figure 6 are based only on small-scale measurements and tests. Such predictions must not be used for predicting the safety of large-scale operations without confirmation on a much larger scale than our time-to-explosion test. Few results from large-scale tests are available for EAK.

Pakulak (11) has run two isothermal 2.5-inch-cylinder tests on EAK. Unfortunately, the assemblies were wrapped with heating tape and insulation, making heat-flow properties difficult to estimate, and the samples were contaminated with rust, which we now know to be incompatible with EAK.

Both of Pakulak's tests were run at 170°C. One test cooked off violently after 12.75 hours, but the other did not cook off in 20 hours. Such behavior could indicate that 170°C was fortuitously near the critical temperature for that size, shape, and composition (including rust), or it could indicate different rust concentrations between the two samples. When our Semenov model is normalized to a T_C of 170°C

at a 6.35-cm diameter, the "Pakulak Expt." curve of Figure 6 is obtained. We believe that the results indicate that a lower activation energy is required to model rust-contaminated EAK than is needed to model pure EAK; however, it appears that even rust-contaminated EAK can be handled safely with normal precautions.

Another large-scale test was run at Los Alamos (12). It was run in a mild-steel container to observe possible interactions with iron and/or rust. The 25-pound charge formed an 8-inch cylinder with length = diameter. The container was covered with a loose-fitting top that contained three radially located thermocouples between the wall and the center. The assembly was preheated at 90°C in an oven for 17 hours to reduce power demands when the experiment was started and run with integral electric heaters.

The sample melted and quickly attained a nearly uniform temperature of about 170-173°C under natural convection. Approximately 3.3 hours later, the temperature at the wall was about 190°C and the temperature at the center was about 184°C; however, there had been some manipulation of power levels, making it difficult to specify accurate equilibrium temperatures.

Without further manipulation, the temperature near the wall went from 190 to 232°C in 20 minutes while the temperature at the center went from 184 to 246°C. Smoke was observed, and the charge burned without violence.

With regard to the 8-inch EAK heating test, the Frank-Kamenetskii model predicts a T_C of 149°C for a system with no convective cooling. The iron-wall Semenov model (Figure 6) predicts a T_C of 182°C. The predicted T_C is exactly in the middle of the experimental temperature range during the self-heating reaction (about 173-190°C); however, it would be extremely useful to know some heat-transfer coefficients for the experimental assembly.

Zinn and Mader (13) presented a method for calculating times to explosion that worked quite well for TNT, RDX, cyclotol, and pentolite at temperatures above their melting points. Although we do not have a measured critical temperature for the 8-inch test, we can use their method by assuming different critical temperatures and comparing calculated times with the observed time (3.3 hours after reaching 170°C). The time constant for the 8-inch geometry ($\tau = a^2 c_p \rho / \lambda$, where c_p is the heat capacity) should be about 20645; therefore, assuming a T_C of 182°C and a wall

temperature of 190°C, the time to ignition should be about 5.4 hours. Assuming a T_C of 160°C and a wall temperature of 180°C, the time to ignition should be about 3.2 hours. The times indicate that none of the Semenov models are completely unrealistic.

Calculated times to explosion for pure EAK are extremely large at temperatures near the critical temperature. The rate curves of Figure 2 show important induction processes; therefore, a long time to explosion is to be expected. Unfortunately, additives and impurities cause a significant shortening of times to explosion; therefore, it is probably not safe to depend on the indicated long times to explosion that would enable operations above the critical temperature for any specific operation.

Depending on the source, we have measured critical temperatures between 230 and 324°C for AN in approximately 1-mm-thick slabs. Experimental time-to-explosion curves in that geometry are shown in Figure 7. Some batch-to-batch variation must be assumed for all of the components of EAK; therefore, it will be important to maintain strict quality control on materials. Routine time-to-explosion tests on small EAK batches formulated from materials proposed for larger batches could provide useful control.

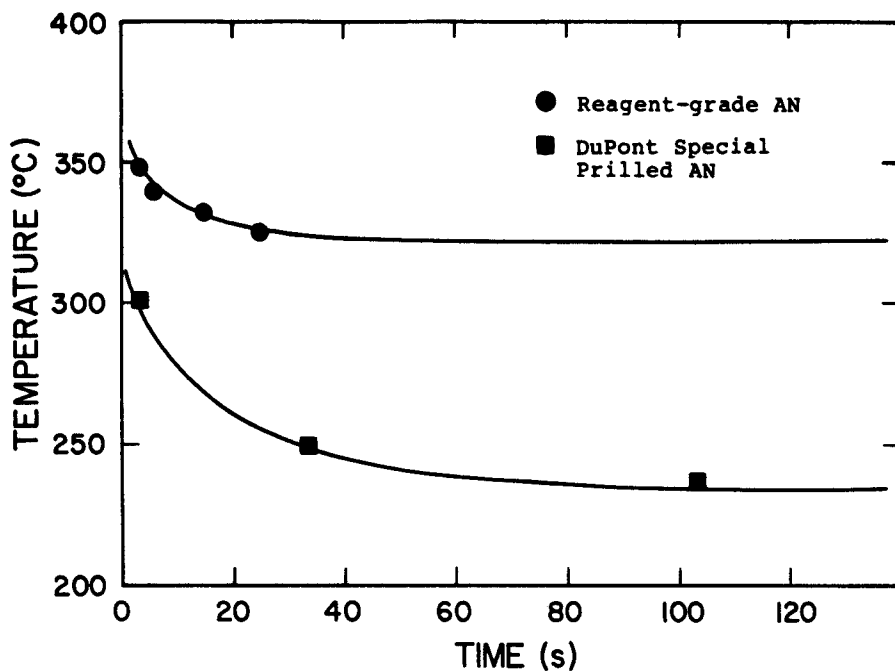


Figure 7. Experimental time-to-explosion curves for different samples of AN.

The EAK/Al System

It has been observed that aluminized EAK is somewhat more sensitive than pure EAK; therefore, we were requested to give some consideration to the results of adding aluminum to EAK. We have taken a somewhat different approach than normal because our limited budget made it impossible to measure an activation energy for the system.

Experimental time-to-explosion data for different EAK/Al mixtures are shown in Figure 8. None of the mixtures showed critical temperatures below that of pure EAK (248°C); however, times to explosion were somewhat shortened. Aluminum acts primarily as a diluent, reducing the effective heat of reaction of the system. The clustering of test results seen in Figure 8 makes it appear possible to use the activation energy measured for pure EAK to produce a preliminary predictive model for EAK/Al mixtures, and that is what we have done.

Best-case critical-temperature predictions according to equation 2 are shown in Figure 9 for different EAK/Al mixtures, and worst-case predictions according to equation 1 are shown in Figure 10. The models are identical to those used for pure EAK, with the exception that both the heat of the reaction and

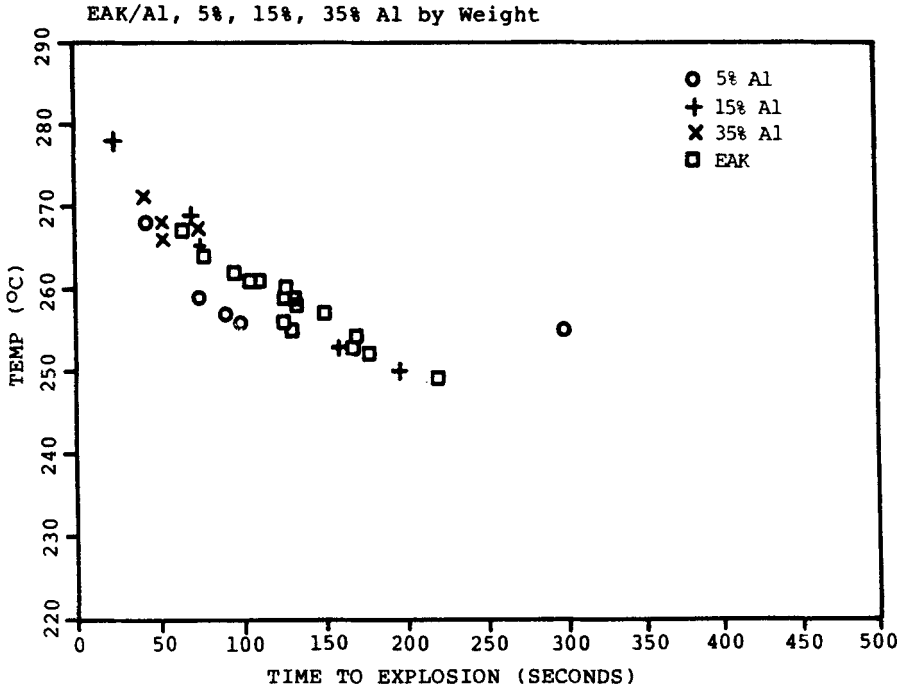


Figure 8. Experimental time-to-explosion measurements for pure EAK and different EAK/Al mixtures. Average sample (slab) thicknesses were the following: EAK, 0.08 cm; 95/5-EAK/Al, 0.084 cm; 85/15-EAK/Al, 0.084 cm; and 65/35-EAK/Al, 0.069 cm.

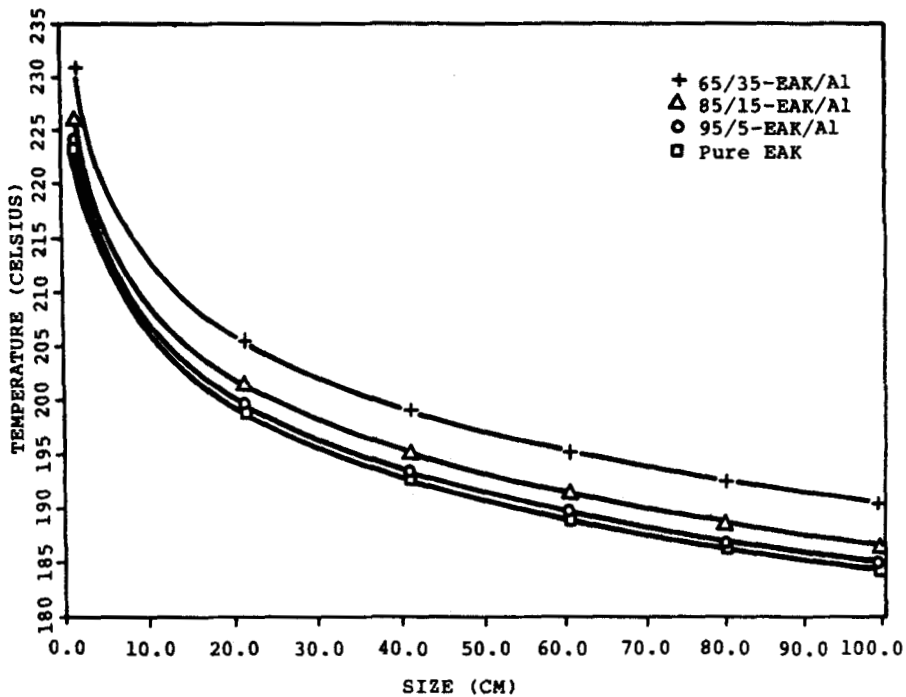


Figure 9. Critical temperature predictive curves for perfectly stirred spheres of EAK and different EAK/Al mixtures (Semenov model). All assume a heat-transfer coefficient of $0.0085 \text{ cal/cm}^2 \cdot \text{s} \cdot \text{K}$.

The curves have all been normalized to their experimental critical temperatures.

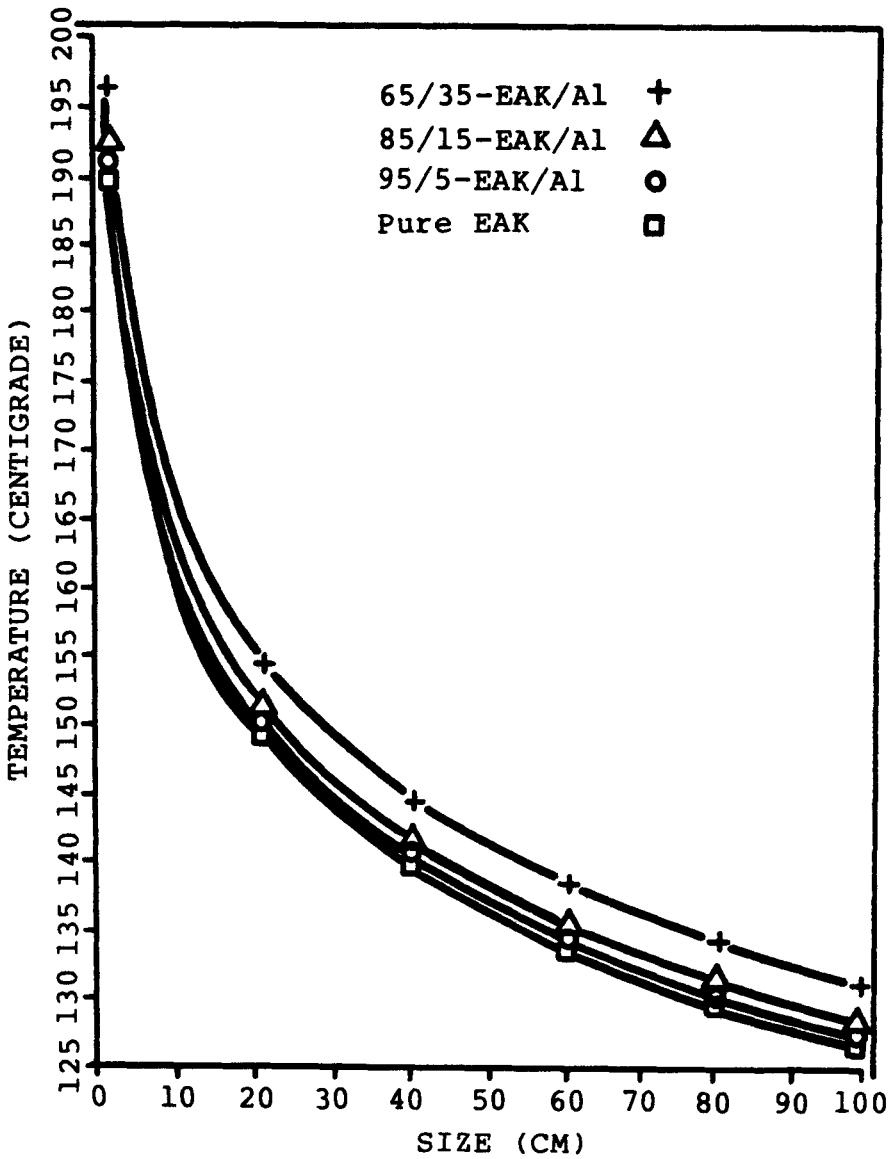


Figure 10. Critical temperature predictive curves for infinite cylinders of EAK and different EAK/Al mixtures under conditions of purely conductive heat flow (Frank-Kamenetskii model).

The curves have all been normalized to their experimental critical temperatures.

the density are reduced by an amount equivalent to the volume percent of aluminum added. The predictive curves are intended to put the thermal-hazard problems of EAK/Al mixtures in perspective: They are not intended to be taken as definitive results. The further sizes get from the experimental sizes the less confidence can be justified in the predictions.

The EAK/Rust System

Figure 11 shows a comparison between experimental time-to-explosion curves obtained from pure EAK and EAK with 15 wt% rust added. Rust both shortens time to explosion and reduces the critical temperature to a significant extent. The critical temperature for EAK/15 wt% rust is estimated to be about 234°C for a 0.074-cm-thick disc.

An attempt was made to determine an effective activation energy for the EAK/rust system within the time and money limitations of the program. It is obvious that the system is significantly different from the EAK/Al system; therefore, it is not valid to assume an unchanged activation energy from that of pure EAK.

Figure 12 shows a comparison among rate curves for pure EAK, EAK/5-wt%-Al, and EAK/15-wt%-rust at the same constant temperature. Rust causes EAK to reach its

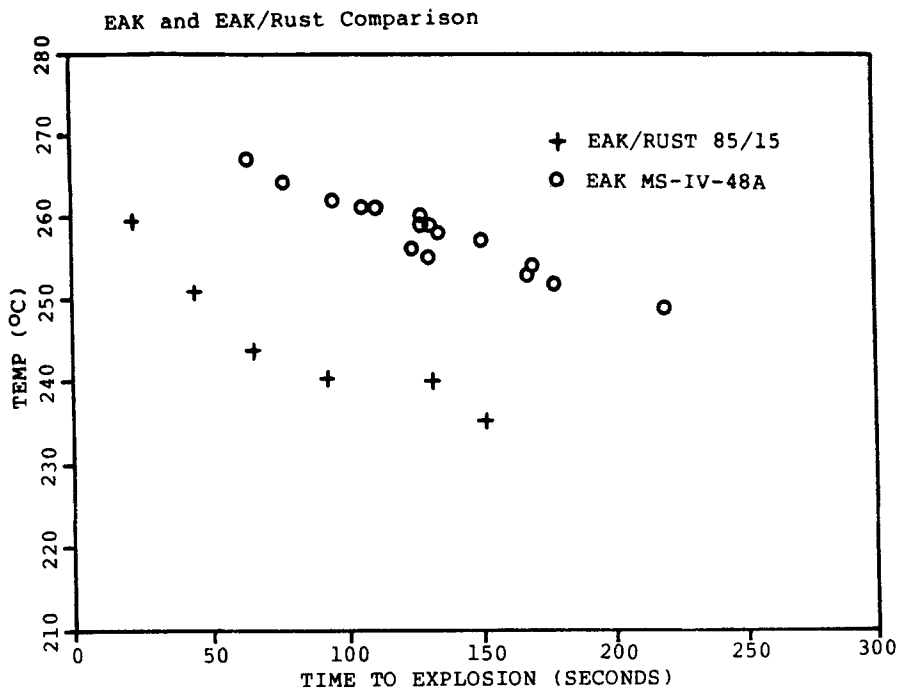


Figure 11. Experimental time-to-explosive curves for EAK (0.08-cm-thick slab) and 85/15-EAK/rust (0.074-cm-thick slab). Rust both shortens time to explosion and lowers the critical temperature of EAK.

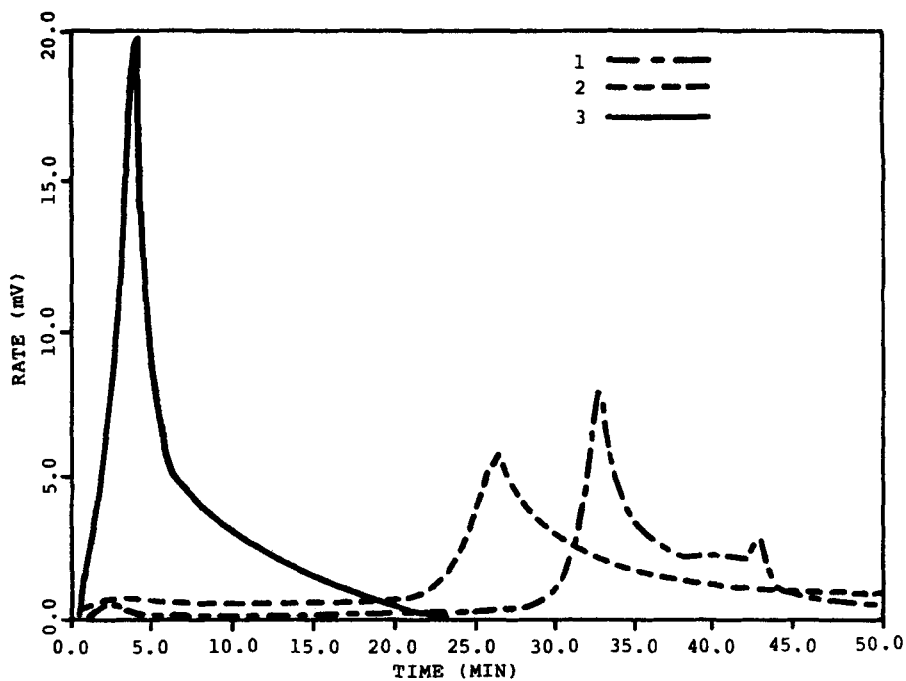


Figure 12. (1) Isothermal rate curve for pure EAK at 490 K.
 (2) Isothermal rate curve for 95/5-EAK/Al at 490 K.
 (3) Isothermal rate curve for 85/15-EAK/rust at 490 K.

The curves have been normalized to 1 mg EAK.

maximum rate much more rapidly than normal. Because time-to-maximum-rate measurements were used to estimate an activation energy for EAK, the same method was used for EAK/rust. An activation energy of 31.6 kcal mole⁻¹ was measured with 15 wt% rust (5 vol%), and a value of 33.5 kcal mole⁻¹ was measured with 55 wt% rust. The temperature coefficient of the rate (activation energy) is not sensitive to the amount of rust. Figure 13 shows a comparison between worst-case predictions obtained from convective and conductive heat-flow models for 85/15-EAK/rust.

With regard to the Pakulak experiment (Figure 6), normal EAK kinetics predict a Semenov critical temperature of about 194°C for his system. The prediction is obviously wrong, because he observed a violent explosion at 170°C. Using the kinetics constants for a sample containing 5 vol% rust ($E = 31600 \text{ cal mole}^{-1}$ and $Z = 4.67 \times 10^{11} \text{ s}^{-1}$), the predicted critical temperature is about 156°C. The thermal stability of Pakulak's sample was almost certainly degraded by rust.

SUMMARY AND CONCLUSIONS

We have made preliminary kinetics measurements on the explosive EAK, and we have suggested worst-case (Frank-Kamenetskii) and best-case (Semenov) models for predicting critical temperatures for charges of

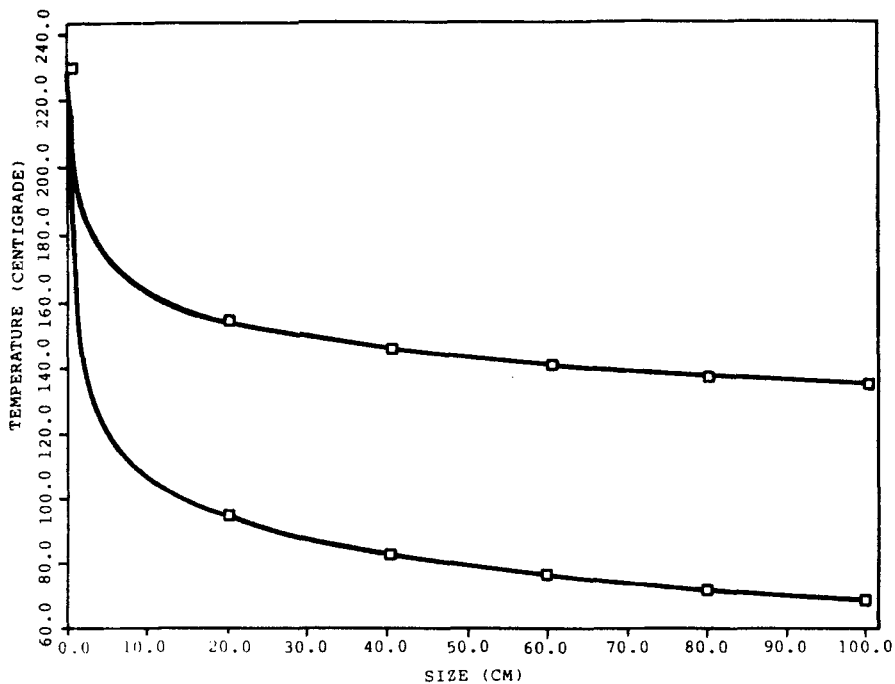


Figure 13. Worst-case critical-temperature predictions for 85/15-EAK/Rust. The upper curve assumes spherical geometry and perfect convective heat flow. The lower curve assumes infinite-slab geometry and purely conductive heat flow. The size, shape, and state of a rust-contaminated zone must be considered in estimating thermal hazards.

different sizes and shapes. The following values are used in the models: liquid density, 1.46 g cm^{-3} ; heat of reaction, 500 cal g^{-1} ; activation energy, $47000 \text{ cal mole}^{-1}$; $2.89 \times 10^{17} \text{ s}^{-1}$; and thermal conductivity, $5 \times 10^{-4} \text{ cal s}^{-1} \text{ cm}^{-1} \text{ K}^{-1}$. A heat-transfer coefficient must be measured or estimated for application of the Semenov model.

The models have been tested with a small-scale time-to-explosion test, and the few existing large-scale tests are discussed. No unreasonable values must be assumed to enable predictions that agree with observed large-scale results; however, our problems with predictions have emphasized the need for accurate, measured values for heat-transfer coefficients.

At their current stage of development, we believe that our models are sufficiently accurate to be used for predicting the thermal hazards of development-scale operations. We do not have sufficient confidence in the models to use them for production-scale operations. Well controlled large-scale tests that can be modeled must be run before EAK is taken into production. Our "best guess" is that equipment safe to use with Comp B will prove to be safe to use with EAK with some margin of safety (assuming purity of components and clean equipment).

Wide variations in thermal stability have been observed with different samples of ammonium nitrate; therefore, we believe that strict control must be maintained on materials used for the formulation of EAK. We suggest control by routine time-to-explosion tests on small-scale formulations made with proposed materials.

Aluminum appears to be compatible with EAK with regard to formulation and casting operations. Critical temperatures are not lowered by addition of aluminum; however, the time required to reach the maximum decomposition rate at any temperature is reduced. Times to explosion are reduced slightly by addition of aluminum. The observed effects of aluminum on the sensitivity of EAK must be considered with the thermal properties in assessing the overall safety of the material.

Rust causes a significant reduction in the thermal stability of EAK. We believe that the activation energy of the rate-controlling process in the rust-catalyzed decomposition of EAK must be within the range of 30 to 35 kcal mole⁻¹. Normal good explosives procedures should obviate any problems with rust.

ACKNOWLEDGEMENT

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GLOSSARY

- α the heat-flow coefficient
- AN ammonium nitrate
- c_p heat capacity at constant pressure
- δ a dimensionless shape factor
- E the activation energy from the Arrhenius equation
- EAK as used in this report, 50/42.5/7.5 wt% EDD/AN/KN
- EDD ethylenediamine dinitrate
- KN potassium nitrate
- λ thermal conductivity
- Q heat of reaction for the process involved in self heating to explosion
- ρ density
- R the gas constant (1.987 cal/mole/K)
- t time
- T_C the critical temperature
- X the fraction decomposed
- Z the pre-exponential from the Arrhenius equation

REFERENCES

- (1) W. Spencer and H.H. Cady, Propellants and Explosives 6, (1981) 99.
- (2) W.F. Meyer, Explosives, Verlag Chemie, New York (1977).
- (3) D.A. Frank-Kamenetskii, Diffusion and Heat Transfer in Chemical Kinetics, Plenum Press, New York, NY (1969).
- (4) N.N. Semenov, Chemical Kinetics and Chain Reactions, Oxford University Press, London (1935).
- (5) R.N. Rogers, Thermochimica Acta 11 (1975) 131.
- (6) D. L. Jaeger, "Thermal Response of Spherical Explosive Charges Subjected to External Heating," Los Alamos National Laboratory Report LA-8332, August 1980.
- (7) A.G. Keenan and B. Dimitriades, Trans. Faraday Soc. 57 (1961) 1019.
- (8) A.J.B. Robertson, J. Soc. Chem. Ind. 67 (1948) 221.
- (9) F. I. Dubovitskii, V.V. Barzykin, and A.G. Merzhanov, Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1124-1126 (1960).
- (10) L.R. Rothstein, Naval Weapons Station, Yorktown, VA, personal communication, October 8, 1982.
- (11) J.M. Pakulak, Naval Weapons Center, China Lake, CA, personal communication, June 22, 1982.
- (12) M.A. Fletcher, Los Alamos National Laboratory, personal communication, June 7, 1982.
- (13) J. Zinn and C.L. Mader, J. Applied Physics 31 (1960) 323.