Medjunarodni naučno-stručni skup sa izložbom
XXIII NAUKA I MOTORNA VOZILA 2011
SCIENCE AND MOTOR VEHICLES
International Automotive Conference with Exhibition
19 - 21 April 2011, Beograd, Serbia

NMV11AutoSim06

Effect of energetic powder additives on fuel drop autoignition at conditions relevant to diesel engine

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ABSTRACT. Recent experimental investigations showed that ultra-dispersed powders of mechanically activated nanocomposite Al–MoO_3 and Mg–MoO_3 particles exhibit anaerobic explosion-type reaction at relatively small heating up to 500–600 K. Therefore thickening of liquid hydrocarbons with such particles can be effectively used for mixture homogenization in transportation engines and decreasing pollutant emissions into the atmosphere. When placed into a hot gaseous flow, thickened-fuel drops can exhibit controlled 'microexplosion' behavior. In this paper, the possibility of thickened-fuel drop 'microexplosion' is examined using a mathematical model of single-component drop heating, evaporation, and combustion.

KEY WORDS: Liquid drop combustion, mechanically activated nanocomposite particles, 'microexplosion.'

INTRODUCTION

The object of the study reported herein is the liquid fuel drop thickened with energetic nanocomposite particles (Figure 1). These particles are composed of metal (Aluminum, Magnesium, etc.) and solid oxidizer (Molybdenum oxide, Teflon, Carbon, etc.). The powder of such particles is prepared using mechanical activation technique (Figure 2). Two powders (metal and oxidizer) are mixed and mechanically milled in a ball mill during a certain time. In the course of milling, one obtains energetic powder with metal and oxidizer particles in close contact with or encapsulated in each other.
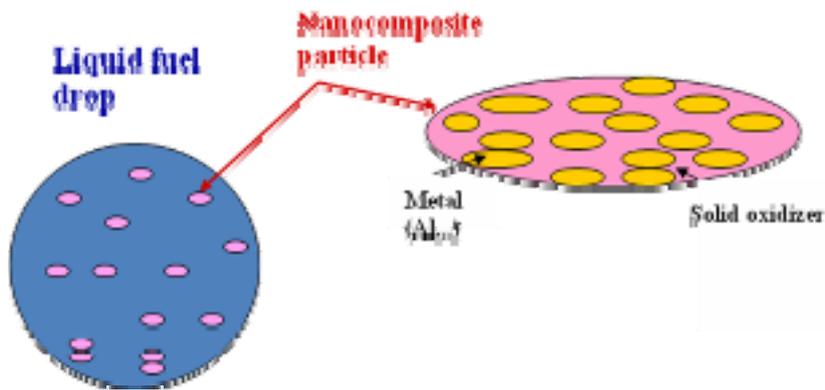
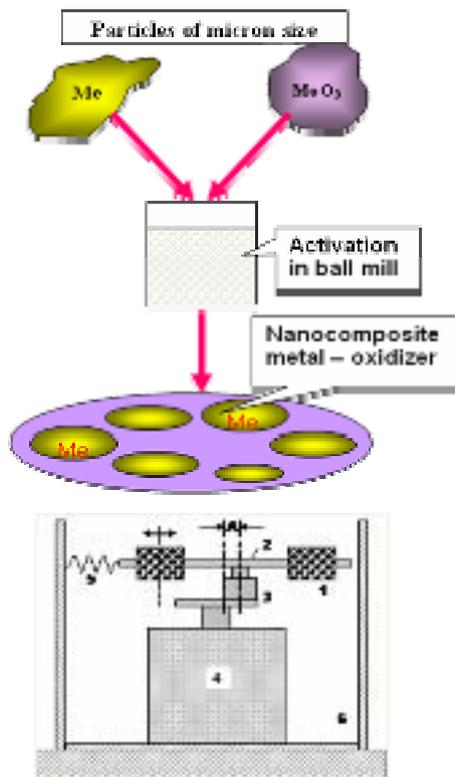Figure 1: Hydrocarbon fuel drop thickened with nanocomposite powder

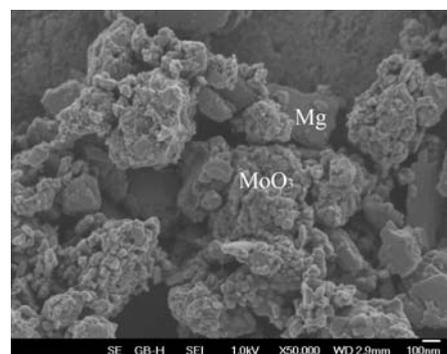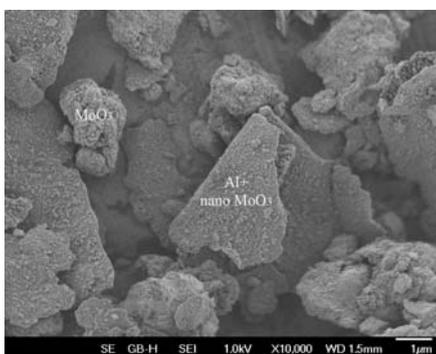Figure 2: Mechanical activation of powders.

Figure 3: Microphotographs of mechanically activated Al–MoO$_3$ (a) and Mg–MoO$_3$ (b) nanocomposite powders prepared using mechanical activation technique.

Figure 3 shows the microphotographs of mechanically activated Al–MoO$_3$ (Figure 3a) and Mg–MoO$_3$ (Figure 3b) nanocomposite powders (Borisov et al. (2010), Frolov et al. (2010)). The Al–MoO$_3$ system contains Al flakes of micron size covered by MoO$_3$ nanoparticles. In Mg–MoO$_3$ system, the size of Mg particles is considerably smaller (about 200 nm) and the contact area between metal and oxidizer is considerably larger than in Al–MoO$_3$ system.

From now on, such powders will be referred to as energetic nanocomposite powders (ENP). Term "nanocomposite" comes from the fact that one or both ingredients are presented by nanosize particles. Such a powder is very reactive. Its relatively small heating results in explosion-like exothermic reaction.

The idea of the study reported herein was to find out whether addition of small amounts of such a powder to liquid fuel can lead to drop 'microexplosion.' To illustrate the drop 'microexplosion' phenomenon, we refer to Figure 4 taken from Law (1998). This figure shows time integrated flame streaks of the freely falling
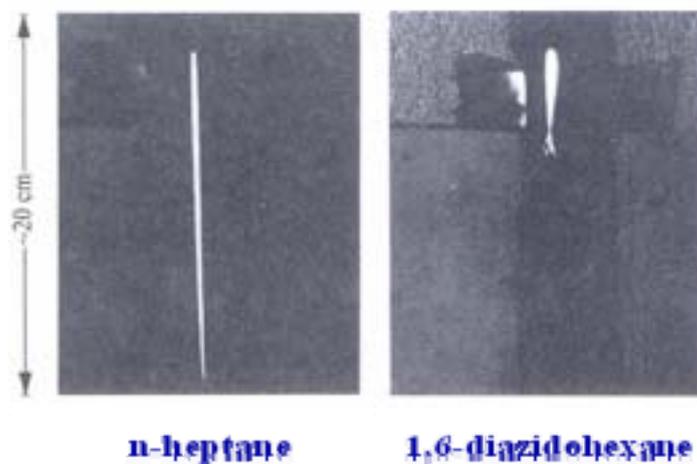

n-heptane   1,6-diazidohexane

Figure 4: Flame streak traced by the burning of the drop stream for different fuels, showing their relative burning intensities and tendencies to microexplode (Law (1998)).

burning drops of n-heptane and diazidohexane. The length of the flame streak is proportional to the drop burning time. Clearly, the lifetime of the second drop is a factor of 3 shorter, which is caused by explosion of the liquid high-explosive drop due to its heating followed by condensed-phase decomposition reactions. Similar microexplosions of drops were observed for hydrocarbon fuel blends and emulsions (see, e.g., Lasheras et al (1981)). The same drop behavior can be expected if one adds ENP to a hydrocarbon fuel.

OVERVIEW OF PREVIOUS EXPERIMENTAL FINDINGS

In our preliminary experimental investigations (Borisov et al. (2010)), powders of mechanically activated nanocomposite Al–MoO$_3$ and Mg–MoO$_3$ particles were shown to exhibit explosion-type anaerobic reaction at relatively small heating up to 500–600 K. The effect of ENP additive to hydrocarbon fuel is presented in Figure 5. Figure 5 shows some experimental results for ignition delays of thickened n-heptane and Diesel oil obtained in static apparatus. Black symbols and lines correspond to neat fuels. Red symbols correspond to fuels with 2.5%(wt.) additive of energetic Mg–MoO$_3$ nanocomposite. One can see that ENP additive becomes effective starting from a certain threshold temperature (red vertical line) which is about 550–570 K for Diesel oil. At temperatures exceeding the threshold value, the ignition delay drops abruptly by about 2 orders of magnitude.

The most important experimental findings reported by Borisov et al. (2010) are:
- even very small additives of ENP can significantly reduce ignition delays of hydrocarbon fuels;

- at temperatures below the threshold value, the ignition delays of thickened fuels differ only insignificantly from the ignition delays of neat hydrocarbon fuels;
- the threshold temperature is independent of the fuel type and is controlled by the ENP properties; and
- burning velocities of thickened-fuel drop suspensions in air at elevated temperatures after their self-ignition in hot spots can be 1.5 to 2 order of magnitude greater than burning velocities of the appropriate hydrocarbon fuels under identical conditions. The flame in such suspensions propagates with acceleration, which would facilitate its run away to detonation.

In addition to the experiments in static apparatus, a series of experiments in research Diesel engine was made. The engine used was the four-cylinder air-cooled Diesel engine operating at a fixed rotation rate (1500 rpm). The engine was operated both with neat Diesel oil and with Diesel oil thickened with 1%, 2%, 3%, and 4%(wt.) Mg–MoO$_3$ nanocomposite additive. The most important findings are:
- the indicating efficiency of the engine operated with the thickened fuel increased by about 10%–11% as compared to operation with neat fuel;
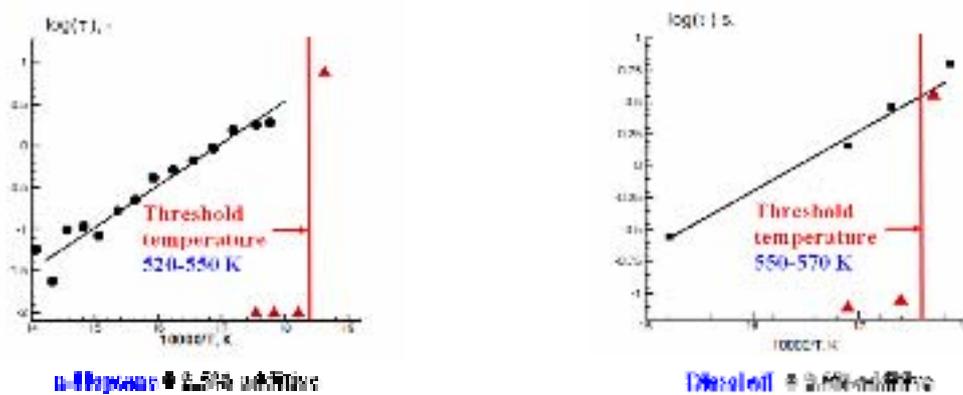

Figure 5: Experimental results for ignition delays of neat (black symbols and lines) and thickened (red symbols) n-heptane and Diesel oil measured in static apparatus (Borisov et al. (2010)).

- the maximum indicating pressure decreased by about 4% as compared to operation with neat fuel irrespectively of the amount of ENP additive; and
- the maximum rate of pressure rise decreased nearly twice as compared to operation with neat fuel.

These findings are illustrated by Figure 6 which shows a set of experimental indicating diagrams for engine operation with neat Diesel oil (solid curve marked by arrow) and with thickened Diesel oil (dashed curves).

In view of these experimental findings, we studied the possibility of thickened-fuel drop 'microexplosion' using a mathematical model of single-component drop heating, vaporization, ignition and combustion reported by Frolov et al (2009). At this stage of investigation, the effect of ENP additive on fuel drop behavior was neglected.

MODEL

The liquid drop is assumed to be a sphere of radius r_s and occupy the region $0 < r < r_s$ at time t. The droplet size is allowed to vary in time due to thermal expansion and liquid vaporization processes. Therefore, r_s is treated as the moving boundary. The continuity equation for liquid is

$$\frac{\partial \rho_d}{\partial t} + \frac{1}{r^2}\frac{\partial}{\partial r}(r^2 \rho_d u_d) = 0$$

where index d relates to liquid, r is the radial coordinate, ρ is the density, and u is the velocity.

Temperature distribution in liquid ($0 < r < r_s$), $T_d(r)$ is governed by the energy equation:

$$c_d \rho_d \frac{\partial T_d}{\partial t} + c_d \rho_d u_d \frac{\partial T_d}{\partial r} = \frac{1}{r^2} \frac{\partial}{\partial r}\left(\lambda_d r^2 \frac{\partial T_d}{\partial r} \right),$$

$$T_d(0,r) = T_{d0}, \quad \left.\frac{\partial T_d}{\partial r}\right|_{r=0} = 0, \quad T_d(t,r_s) = T_g(t,r_s),$$

where T is the temperature, c is the specific heat, and λ is the thermal conductivity.

The mass concentration of liquid vapor (index v) at the drop surface is

$$Y_v = \frac{P_v}{P} \frac{W_v}{\overline{W}},$$

where P is the pressure, W is the molecular mass, and bar denotes the mean value.

The gas phase (index g) is assumed to occupy region $r_s < r < R$, where R is the half-distance between
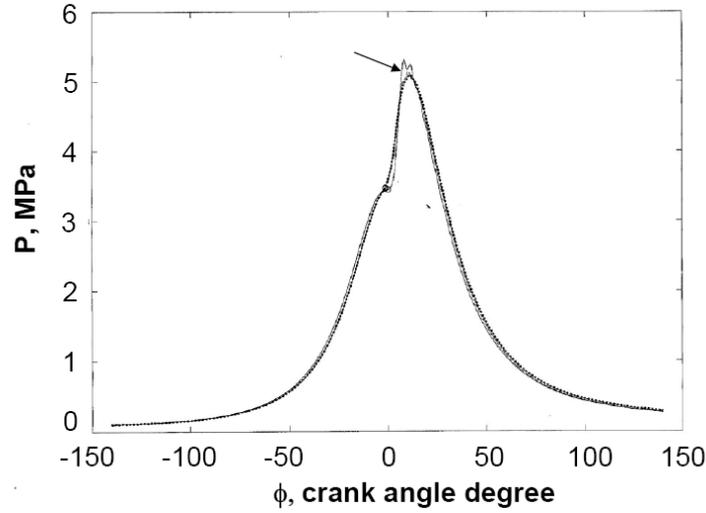

Figure 6: Experimental indicating diagrams for engine operation with neat Diesel oil (solid curve shown by arrow) and with Diesel oil (dashed curves) thickened with 1%, 2%, 3%, and 4%(wt.) Mg–MoO$_3$ nanocomposite additive.

drops in gas–drop suspension. The gas flow around the drop is governed by the continuity equation

$$\frac{\partial \rho_g}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r}(r^2 \rho_g u_g) = 0,$$

$$\rho_d \left.\left(u_d - \frac{\partial r_s}{\partial t}\right)\right|_{r=r_s} = \rho_g \left.\left(u_g - \frac{\partial r_s}{\partial t}\right)\right|_{r=r_s},$$

species continuity equation

$$\rho_g \frac{\partial Y_j}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r}(\rho_g r^2 Y_j V_j) - \rho_g u_g \frac{\partial Y_g}{\partial r} + \omega_{gj}$$

$$Y_j(0,r) = Y_{j0} \quad j = 1,2,...,N,$$

$$-\rho_d u_i \beta_j \big|_{r=r_s} = \rho_g Y_j \left(u_g - \frac{\partial r_m}{\partial t}\right) + \rho_g Y_j V_j \big|_{r=r_s},$$

$$\left.\frac{\partial \overline{W} Y_j}{\partial r}\right|_{r=R} = 0, \quad j = 1,...,N$$

$$X_j = Y_j \overline{W} / W_j$$

$$\frac{\partial X_j}{\partial r} = \sum_{k=1}^{N} \left(\frac{X_j X_k}{D_{jk}} \right) (V_k - V_j)$$

$$\omega_{gj} = W_{gj} \sum_{k=1}^{L} (v_{j,k}^{//} - v_{j,k}^{/}) A_k T_g^{n_k} \exp\left(-\frac{E_k}{RT_g} \right) \prod_{l=1}^{N} \left(\frac{Y_{gl} \rho_g}{W_{gl}} \right)^{v_{l,k}^{/}}$$

$$\beta_j = 1 \text{ at } j = v$$

$$\beta_j = 0 \text{ at } j \neq v$$

and energy equation

$$c_{pg} \rho_g \frac{\partial T_g}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(\lambda_g r^2 \frac{\partial T_g}{\partial r} \right) - c_{pg} \rho_g u_g \frac{\partial T_g}{\partial r} + \Omega$$

$$T_g(0,r) = T_{g0}$$

$$T_g(t,r_s) = T_d(t,r_s), \quad \left. \frac{\partial T_g}{\partial r} \right|_{r=R} = 0$$

$$\Omega = \sum_{k=1}^{L} H_k A_k T_g^{n_k} \exp\left(-\frac{E_k}{RT_g} \right) \prod_{j=1}^{N} \left(\frac{Y_{gj} \rho_g}{G_{gj}} \right)^{v_{j,k}^{/}} ,$$

where index 0 denotes the initial value, Y_j is the mass fraction of species j; D_j is the diffusion coefficient for species j; ω_j is the rate of variation of mass fraction of species j due to chemical reactions; Ω is the chemical heat source; A_k, n_k, E_k, and H_k are the preexponential factor, power exponent, activation energy, and heat effect of the kth reaction; N is the number of species; L is the number of reactions, respectively.

In addition to above equations, the boundary condition for tailoring temperature fields in liquid and gas at $r = r_s$

$$\lambda_d \frac{\partial T_d}{\partial r} - \frac{\rho_{di} u_i L_v}{W_v} = \lambda_g \frac{\partial T_g}{\partial r} \quad ,$$

equation of state for the gas phase

$$\rho_g = \frac{P \overline{W}}{R^o T_g} ,$$

and the condition of constant pressure

$$P = P_0 = const$$

are specified. Here, L_v is the latent heat of vaporization and R^o is the universal gas constant.

Molecular transport processes in liquid and gas phases as well as the corresponding specific heats are taken from Reid et al (1977).

To study ignition and combustion of hydrocarbon fuel drops in air and oxygen, the overall 5-step oxidation mechanism of Frolov et al (2009) for n-tetradecane was used.

The set of governing equations was integrated numerically using nonconservative finite-difference scheme and adaptive moving grid. The computational error was continuously monitored by checking balances of C and H atoms as well as energy balance at each time step.

RESULTS OF CALCULATIONS

In the calculations, ignition procedure simulated the ignition process in Diesel engines, i.e., fuel drops were instantaneously placed in hot air initially at temperature T_{g0} and pressure P_0. The calculations were made for n-tetradecane drops of different initial radii r_{s0} at different T_{g0} and P_0. The results of calculations for n-heptane were reported earlier by Frolov and Frolov (2010).

The necessary condition for drop microexplosion is intuitively simple: the liquid temperature should be greater than the characteristic ENP explosion temperature ($\sim$570 K for Mg–MoO$_3$ additive). Since the temperature distribution in the liquid drop is nonuniform, one could expect the existence of some sufficient conditions for drop microexplosion. Despite the sufficient conditions cannot be formulated within the frame of the present model, it allows estimating the time taken for the drop surface (τ_s) and drop center (τ_c) to heat up to the ENP explosion temperature. Such estimates could provide the quantitative information on the possibility of thickened-drop microexplosion in terms of all governing parameters (e.g., drop size, gas pressure, temperature, etc.). Clearly, when the drop lifetime τ_l exceeds τ_s ($\tau_l > \tau_s$ is the necessary condition for microexplosion), the probability of drop microexplosion increases and at $\tau_l > \tau_c$ it is expected to be high.

As an example, Figures 7 and 8 show the predicted time histories of temperature at the n-tetradecane drop surface (solid curves) and in the drop center (dashed curves) at $P_0 = 10$ bar (Figure 7) and 20 bar (Figure 8) and air temperature 900 K (characteristic of Diesel engine). Tetradecane was used to simulate Diesel oil. At pressure 10 bar, liquid reaches the characteristic explosion temperature ($\sim$570 K for Mg–MoO$_3$ additive) of ENP only at the end of drop lifetime ($\tau_l \approx \tau_s$). At pressure 20 bar, the time taken for the n-tetradecane drop to heat up to the characteristic ENP explosion temperature varies from 0.2 ms (τ_s) to 0.9 ms (τ_c). At higher pressures, both times τ_s and τ_c are getting even shorter. These results are directly relevant to the behavior of thickened-fuel drops of Diesel oil in Diesel engine (see above) and demonstrate a possibility of drop microexplosion during engine operation.
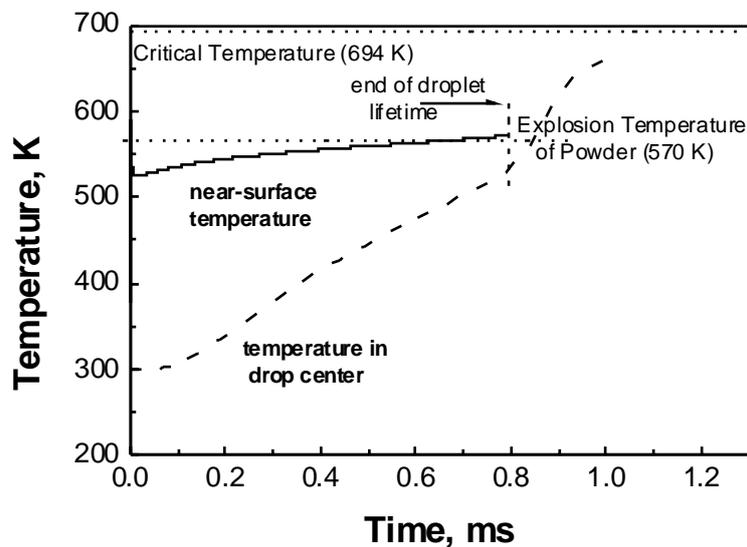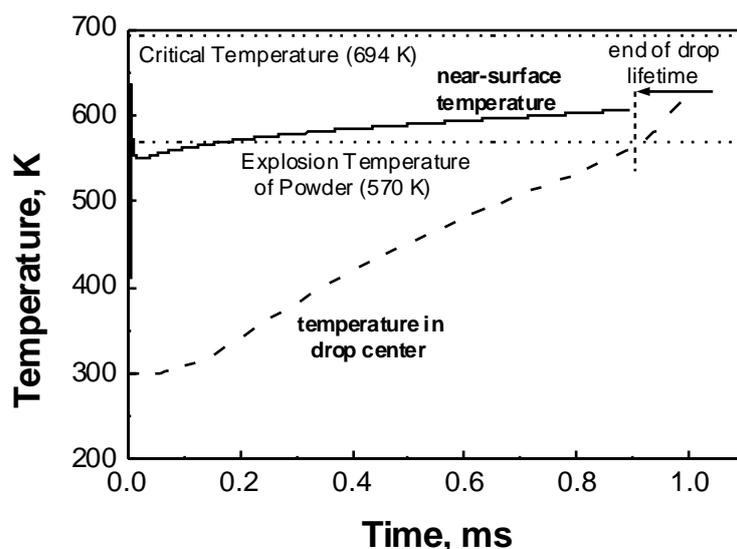

Figure 7: Predicted histories of gas temperature at the surface of burning n-tetradecane drop (solid curve) and liquid temperature in the drop center (dashed curve) at pressure 10 bar ($r_{s0} = 15\,\mu m$, $T_{g0} = 900\,\mathrm{K}$).

Figure 8: Predicted histories of gas temperature at the surface of burning n-tetradecane drop (solid curve) and liquid temperature in the drop center (dashed curve) at pressure 20 bar ($r_{s0} = 15\,\mu m$, $T_{g0} = 900\,\mathrm{K}$).

CONCLUSIONS

Characteristic times of thickened-fuel drop "microexplosion" have been estimated based on the mathematical model of liquid drop heating, vaporization, ignition, and combustion. It has been shown that in Diesel engine conditions, thickened-fuel drops most probably exhibit "microexplosion" phenomenon. Drop 'microexplosion' could be a reason of increased engine efficiency due to mixture homogenization in our experiments reported earlier.

ACKNOWLEDGMENTS

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