INHIBITION OF PREMIXED METHANE-AIR FLAMES
BY SUBMICRON WATER MISTS

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INTRODUCTION

The ban on production of halons has prompted renewed interest in the use of water as a fire suppression agent. Since water is ubiquitous, nontoxic, environmentally benign, and has a high heat capacity per unit mass, it is in many respects an ideal fire suppression agent. Since water is primarily a thermal agent, the possibility exists to enhance its suppression properties by adding an agent that acts chemically. Furthermore, many highly efficient chemical suppressants contain metallic elements, which in most cases form water-soluble salts. Water thus can be used as a delivery mechanism for fire suppressants that are solids at room temperature. Nevertheless, water is a liquid at ambient temperature rather than a gas like Halon 1301 and current fluoro-carbon alternatives. Many engineering issues thus arise concerning droplet size distribution, delivery into and throughout the space to be protected, and complexity of the generation system.

Current fire suppression systems based on water use far more agent than should be required based on a comparison of its sensible enthalpy with that of nitrogen or carbon dioxide. In attempting to broaden the range of fire protection applications for which water can be used, it is desirable to determine to what degree the effect predicted based on water's thermal properties can actually be achieved under favorable conditions. This study focused on characterizing the inhibition effectiveness of water by using the burning velocity of a premixed CH_4-air flame as a metric for suppression. Also, preliminary studies were conducted with aqueous NaOH solutions, to determine if water can be used as a delivery method for chemical suppressants that form water soluble compounds. The liquid suppressants were delivered to the flame as mists, characterized by very small droplets (d < 0.5 μm).

The laminar burning velocity is a fundamental constant of a flammable gas mixture and as such the reduction in laminar burning velocity is frequently used as an indicator of the effectiveness of an inhibiting agent [1-5]. There exist a variety of methods to measure laminar burning velocities [6]. We employed the total area method, a widely used technique due to its relative simplicity. The conical flame area was measured using both visible emission and Schlieren techniques. The degree to which water achieved its inhibition potential, based on thermodynamic properties, was gauged through comparison with measurements performed using the gaseous thermal agents N_2 and CF_4. The N_2 and CF_4 measurements also served as benchmarks to validate the experimental technique through comparison with data from previous studies.

EXPERIMENTAL PROCEDURE

A tubular burner apparatus was used to establish a premixed methane-air flame at atmospheric pressure. The nozzle exit diameter was 5.4 mm, and the burner was cooled with water at 22 °C. The burner had provisions for a co-flow; however, none was used for these measurements. Stoichiometric flames were stabilized on the burner for a range in total gas flow rates between 820 – 1740 ml/min (T = 294 K, P = 760 Torr) using mass flow control devices. Laboratory supply air was filtered and dried to remove oil, water, and particulates larger than 0.1 μm in diameter. The relative humidity of the filtered air stream was measured to be less than 5%. Methane (Matheson, UHP grade) was used as the fuel gas.

Burning velocities were measured using the total area method as described by Andrews and Bradley [6]. In this method, the burning velocity is obtained by dividing the total volumetric flow rate of the reactants by a measured flame area. Several methods are commonly used to image a flame surface, from which an area can then be determined. These methods include direct photography of the luminous flame surface. Schlieren. and shadowgraph techniques. Each method captures a different flame surface, and, as *a* result, the absolute burning velocity is *a* function of the method used. Our interest was primarily focused on measuring the reduction in burning velocity relative to the uninhibited case, and not measuring absolute burning velocities. We imaged the conical flame using both direct photography of the luminous surface and the Schlieren technique. The flame surfaces were imaged with a digital camera in a 640 x 480 pixel array. Images were captured and averaged over a period of approximately 4 sec (20 samples) using custom designed software. A sixth-order even polynomial was fit to each image and integrated to give the flame surface area. Integration was performed from the flame cone axis to a radius of 0.35 cm; this was larger than the radius of the burner at the exit plane (0.27 cm). The larger radius was chosen to match the furthest extent of visible flame zone. The measured flame area was very sensitive to the maximum radius used in the data analysis. Performing integration to a radius equal to that of the burner (0.27 cm) resulted in an increase in the calculated burning velocity of approximately 45% from the value obtained when the integration limit was set at 0.35 cm. However, since **all** burning velocity measurements were normalized by an uninhibited burning velocity measured under the same conditions. the sensitivity to this parameter was reduced significantly. For the same change in radius (0.35 cm to 0.27 cm), the maximum difference in the normalized burning velocity was less than 10% over the entire range of flow rates. The average uninhibited burning velocities measured with the integration limit set to 0.27 cm and 0.35 cm. respectively, were 40.4 cm/s and 27.9 cm/s.

Water mist was delivered to the flame with the reactant mixture. A portion of the air stream was passed through an atomizer that generated a polydisperse distribution of sub-micron sized water droplets, which were entrained in the flow. **A** schematic of the experimental configuration is shown in Figure 1. The pressurized air stream flowed through a small orifice (343 μm), produc-ing a high velocity jet. Water was drawn from a reservoir through a small tube and broken into droplets by the air stream. Larger droplets were impacted against a wall and returned to the reservoir: only the droplets small enough to remain entrained in the flow were carried from the atomizer. The atomizer was calibrated by measuring the change in mass of the water reservoir with time for a fixed air flow rate.

Atomizer specifications state a mean droplet diameter of 0.35 μm for the recommended air flow rate of 3.0 SLPM using **a** 343 μm orifice (Designated "Pinhole" in Figure 1). This flow rate was too high to stabilize a stoichiometric flame on the 5.4 mm nozzle. Experiments showed that reducing the flow rate to a range where a stoichiometric flame could he stabilized resulted in *a* significant reduction in the performance of the atomizer. Consequently, a portion of the air flow from the atomizer was bled to a dump stream with **a** calibrated rotameter to measure the flow rate of the unused gas. One difficulty in controlling the water concentration using this configura-tion and metering valves was that the water tended to collect in large droplets that did not get carried to the flame. Alternatively, controlling flow rates by varying the flow resistance through added tube lengths introduced more surface area for droplets to collect on the tubing walls. Tube lengths between the droplet generator and the burner were minimized to eliminate droplet agglomeration on the walls. As a result, the range of concentrations achievable for water was smaller than that for the gaseous agents.
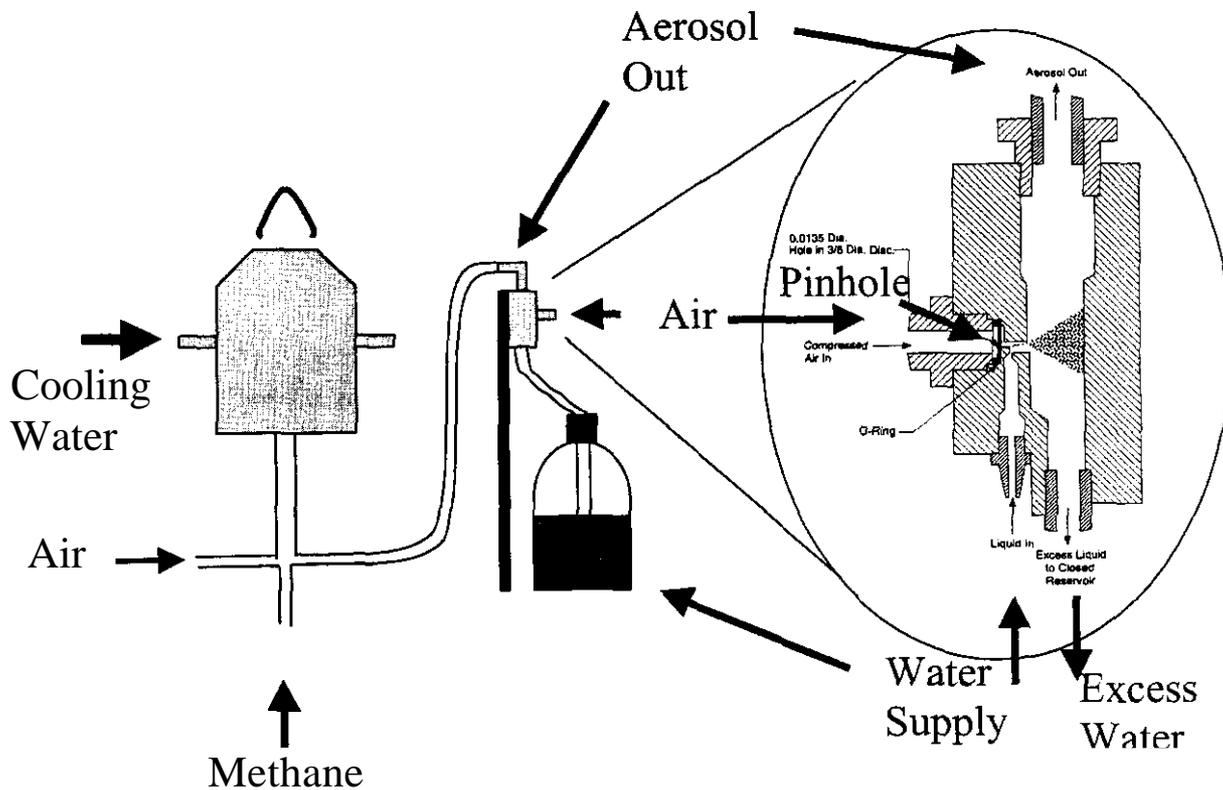
Figure 1. Schematic of experimental configuration. Enlarged image is from TSI Instruction manual, Part Number 133076 – Rev. F (used with permission).

Due to the difficulties discussed above, an alternative method that proved successful was used to control the flow of gases and water mist to the burner. To achieve a similar pressure drop and flow velocity through the orifice at lower flow rates, and thus maintain a similar droplet size distribution, the 343 μm orifice was replaced with a 150 μm orifice. The smaller orifice produced a satisfactory mist at flow rates as low as 650 sccm. This eliminated the need for a dump stream and the complications associated with the previous method. At the same time, the range of achievable water mist concentrations was increased. A separate stream of dry air was added to the reactant mixture downstream of the atomizer to dilute the water concentration; fuel was added to maintain stoichiometric conditions. While the change in configuration of the atomizer may have changed the droplet size distribution, the droplets were still small enough to be completely consumed by the flame. This was confirmed by laser scattering measurements downstream of the flame. Results using both atomizer configurations were in good agreement and are presented together here.

Modeling studies [7] generally have found that suppression efficiency is largely independent of droplet size as long as the size is <30 microns. This is two orders of magnitude larger than the nominal droplet size used in our study. Our purpose in using droplets of this size was to measure suppression by liquid water in the small droplet limit, in which droplets follow the local gas flow and evaporate completely before leaving the flame. While the droplet sizes may have varied from the nominal value, this is unlikely to have influenced the burning velocity unless the size had increased by a highly improbable factor of 50 or more.

Water mist in the reactant stream was monitored by scattering at 90 deg from a Helium-Neon laser (0.6328 μm) with a photomultiplier tube (PMT). The laser was chopped mechanically at 42 Hz. and a reference beam was split off before passing over the burner. The reference beam intensity was monitored by a photodiode. Both the PMT and reference signals were integrated over a period of 30 cycles and the scattering intensity was taken as the ratio of these averaged DC voltages. The beam was positioned horizontally in the small gap between the top surface of the burner nozzle and the luminous flame cone. To monitor the water mist and obtain a simultaneous flame surface area measurement, the flame image was recorded through a filter that blocked the He-Ne scattering.

Although the droplet sizes in the mist were too small to measure using optical techniques (e.g., Phase Doppler Anemomerry), the scattering intensity was used to identify the presence of liquid phase in the reactant stream. The scattering intensity showed an inverse correlation with the addition of dry gas (air + fuel) to the reactant stream, indicating that the concentration of water in the liquid phase decreased as the fraction of added dry gas increased. The reduction in scattering intensity was greater than that which could be attributed to dilution, indicating that a portion of the liquid was evaporating prior to reaching the flame.

The heat of vaporization for water accounts for approximately one-third of its sensible enthalpy over a temperature range from 298 to 2230 K, the adiabatic flame temperature of stoichiometric methane/air. In our experiment. some vaporization of the water droplets undoubtedly occurs before they reach the flame zone. In the absence of energy transfer from the surroundings, the inhibition effect of thermal agents, of which water is one, is independent of the location of heat absorption relative to the flame [8]. The residence time of the air + droplet stream between the droplet generator and the flame is approximately 1-2 sec, comparable to the time scale expected for thermal equilibration. It is not feasible to saturate the air entering the droplet generator with water vapor, because there is a large pressure drop, so the air exiting the generator still would not be saturated. Because the amount of evaporation clearly will depend on experimental conditions and is not easily measured in situ, its effect on the burning velocity is difficult to explain.

RESULTS AND DISCUSSION

To establish the validity of the experimental procedure, measurements were performed on flames inhibited by N_2 and CF_4. Results were compared with earlier studies [1, 4]. Both N_2 and CF_4 are gases at room temperature, which greatly simplifies their delivery to the flame as compared with the delivery of a condensed phase agent. This is retlected in the agreement seen between the data sets in Figure 2. The open points in this figure were taken from a recent experimental study [1], which utilized a procedure similar to the one described here. Also shown are exponential expressions that were fit to PREMIX [9] calculations from Noto et al. [4] and calculations for N_2 inhibited flames carried out in the present study using PREMIX with GRI-Mech. [IO].

To evaluate the inhibition effectiveness of water mist with the other agents under investigation, a comparison was made based on the mass of agent required to reduce the laminar burning velocity. Linear least squares fits were applied to plots of the burning velocity measurements as a function of the amount of agent added. These fits were used to estimate the inhibitor concentration required to reduce the laminar burning velocity by 20% from the uninhibited case. Table I summarizes the results. Column 2 lists the sensible enthalpy per unit mass required to raise the temperature of each agent from 298K to 2200K (the approximate final flame temperature of stoichiometric methane/air with a small amount of *an* inert agent added). The value for liquid
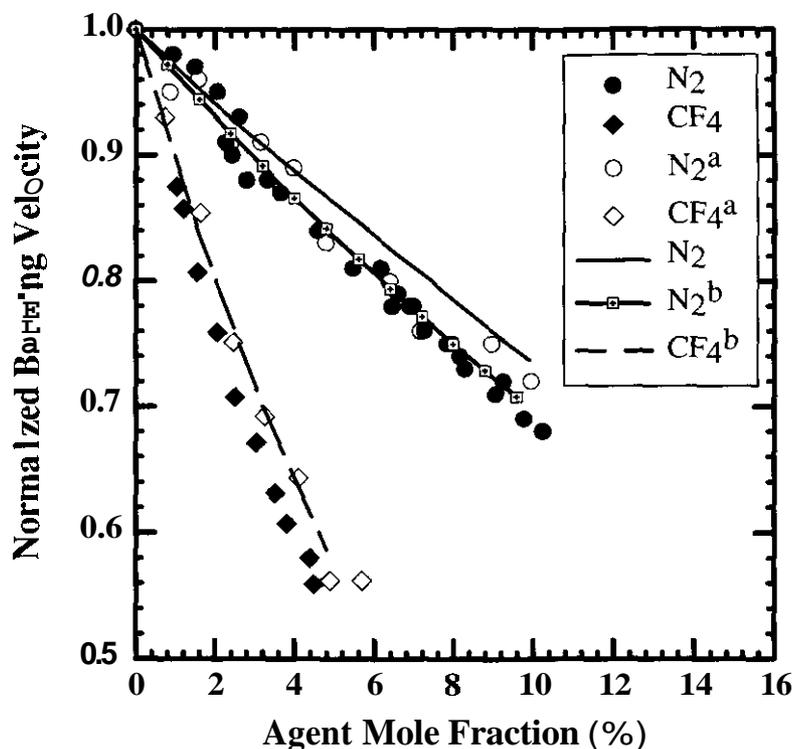
Figure 2. Premixed methane-air burning velocity as a function of agent mole fraction, normalized by the uninhibited burning velocity. Closed points represent measurements from present study, open points (a) are from [1]. Solid line shows calculations from the present study using PREMIX with GRI-Mech. Dashed line and line with square/cross (b) are from [4].

water, including the heat of vaporization, is roughly 3.5 times higher than that for N_2, CF_4 and CO_2. Although CO_2 is not listed in Table 1, it has a sensible enthalpy ($H_f^{2200K} - H_f^{298K} =$ 2.4 kJ/g) [11] close to that of N_2 and CF_4. Additionally, the extinction mass fraction for heptane cup-burner measurements was found to be similar for N_2, CF_4, and CO_2 [12]. Since these agents exhibit predominantly thermal inhibition characteristics, one would expect a similar relationship to exist between the concentrations required to bring about a reduction in burning velocity. Column 4 shows that, on a mass basis, the concentration of water mist required to reduce the burning velocity by 20% was 30–35% of the concentrations required for N_2 and CF_4.

Table 1 shows that the concentration of water mist required for a 20% reduction in burning velocity is comparable to the estimated concentration for CF_3Br. Previous studies [13, 14] have shown that, in non-premixed flames, Halon 1301 (CF_3Br) is 2–2.5 times more effective at extinguishing flames than N_2 on a mass basis. A similar ratio of efficiencies was found in a modeling study of premixed methane-air flames [6]. These findings, in conjunction with our measurements, indicate that water mist can be at least as effective an inhibitor as CF_3Br on a mass basis. This is significant because water acts primarily as a physical suppression agent while CF_3Br has a large chemical inhibition component [16].

Sheinson et al. [12] determined that the sensible enthalpy from 300 to 1600 K per mole O_2 for an agent at the extinction concentration is comparable for most physical agents. The value of 1600 K was used because this represents a typical **peak** temperature of a nonpremixed flame at

extinction, whereas the final flame temperature is a more appropriate metric for flame velocity reduction in a premixed flame. This approach applies to premixed flames. as demonstrated by Figure 3. which plots results of PREMIX calculations for stoichiometric methane/air flames inhibited by nitrogen, CF_4, and water vapor. For all three agents, the burning velocities as a function of the adiabatic flame temperature nearly coincide, indicating that the flame speed depends only on the adiabatic temperature, not on which agent is used. Although the analogous calculation cannot be done for liquid water using the PREMIX code, the thermal effect of adding water in the liquid phase can be taken into account by including the heat of vaporization along with the sensible enthalpy
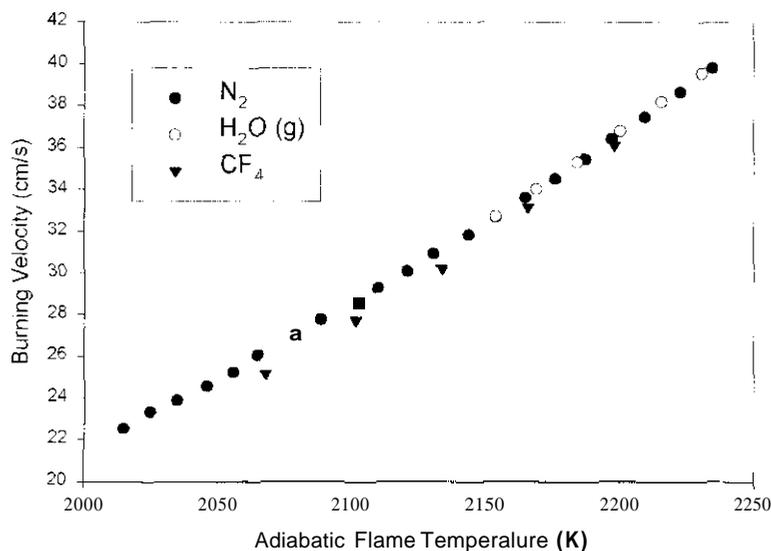

Figure 3.   PREMIX calculations of burning velocities of stoichiometric methane/air mixtures inhibited by various concentrations of nitrogen. CF_4, and water vapor, plotted as a function of the adiabatic flame temperature.

To apply this formalism, we have calculated (Column **6**) the sensible enthalpy per mole O_2 for the agent concentration which causes a 20% burning velocity reduction. Comparison of the values in Column 6 shows that the value for water obtained for the nominal 0.35 μm droplets in this study lies between that for N_2 and CF_4. Thus, based on a comparison of its thermal properties water mist can contribute flame inhibition comparable to that of inert gaseous agents. The significantly lower sensible enthalpy per mole O_2 that is seen for CF_3Br is an indication of a strong chemical inhibition component.

Normalized burning velocity is plotted in Figure 4 on a mass basis for added water mist. N_2, CF_4, and CF_3Br. **As** expected based on the thermodynamic properties listed in Table 1, N_2 and CF_4 exhibit similar inhibition characteristics. Additionally, the water mist effectiveness compares favorably with CF_3Br modeled data [6, 16].
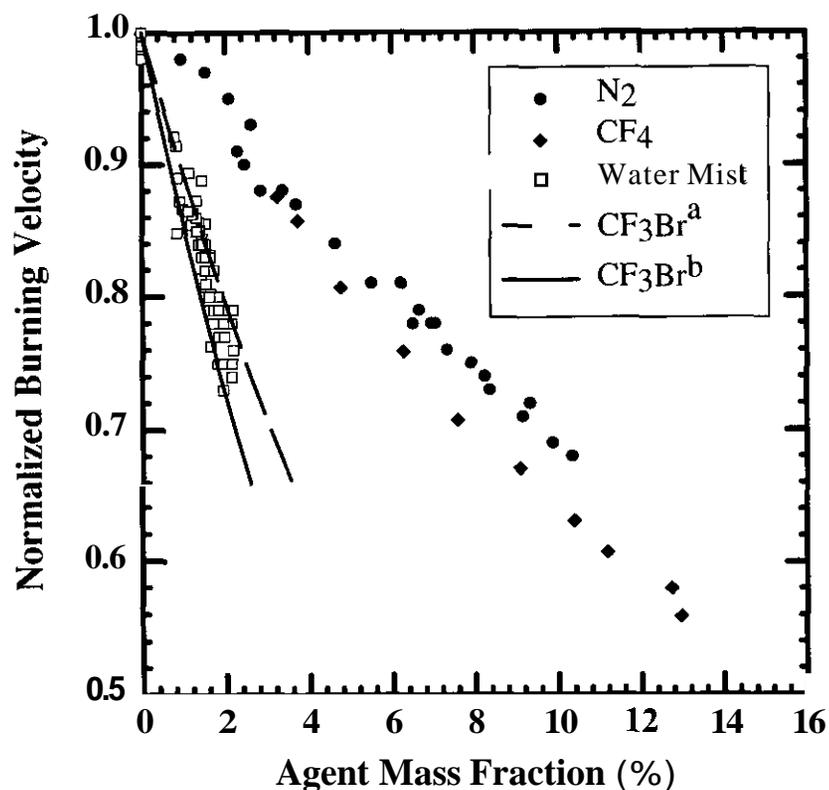
Figure 4. Premixed methane-air burning velocity as a function of agent mass fraction, normalized by the uninhibited burning velocity. Dashed line (a) is from [4]; solid line (b) is from [16].

TABLE 1. COMPARISON OF THERMAL PROPERTIES AND SUPPRESSION EFFICIENCIES FOR N_2, CF_4, WATER MIST, AND CF_3BR.

Agent	$(H_f^{2200K} - H_f^{298K})^a$ KJ/g	$(H_f^{2200K} - H_f^{298K})^a$ kJ/mol	Mass Fraction	Mole Fraction	$(H_f^{2200K} - H_f^{298K})* (X_{agent}/X_{O2})$ (kJ/mol)
N_2	2.3	63	6.3 ± 0.1	6.2 ± 0.1	21.9 ± 0.5
CF_4	2.1	184	5.5 ± 0.1	1.9 ± 0.03	18.2 ± 0.5
H_2O (l)	7.1	127	1.8 ± 0.2	2.7 ± 0.2	18.4 ± 1.5
CF_3Br	1.3	189	1.9^b	0.4^b	4.1

[a] Calculated from data in [10]

[b] Data from [4]

NOTE Columns 2 and 3 list the change in sensible enthalpy of each agent for a range in temperature from 298k to 2200k. The value *for* water mist includes the heat of vaporization at one atmosphere. Columns 4 and 5 list the mass and mole fractions of the total flow, respectively, for the conditions required to reduce the burning velocity by 20% from the uninhibited case. Column 6 is the product of column 3 with the ratio of agent mole fraction (x) to O_2 mole fraction for the condition where the burning velocity is reduced by 20% from the uninhibited case. Uncertainties are based on scatter *in* the data.

SUMMARY

Measurements performed in this study indicate that water mist can be as effective as CF_3Br at inhibiting flames on a mass basis. Water mist was shown to be approximately 3.5 times more effective by mass than inert agents, N_2 and CF_4, at reducing the burning velocity of premixed methane-air flames. The thermal capacity of water mist can be used effectively in comparison with gaseous thermal agents. given suitable conditions. Future research will investigate the effectiveness of aqueous solutes at reducing the burning velocity.

ACKNOWLEDGMENTS

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