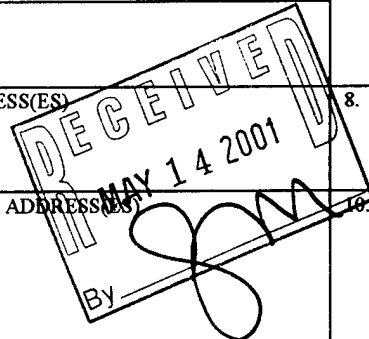


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I. Foreword

This report describes research on fluorescent diagnostics carried out by students who received support under ASSERT grant DAAH04-94-G-0203. This ASSERT grant was in place in conjunction with two other U.S. ARO grants, DAAH04-94-G-0020 (5/15/94-5/14/97) and DAAG055-97-1-0265 (5/15/97-03/01/01). The final report for the former was filed in 1997. The final report for the latter will be filed within the next month, and it will contain a full report on the progress in the development of fluorescent diagnostics for droplets and sprays during that time period.

II. List of Illustrations

1. Calibration Curve for Fluorescent Diagnostic for Fuel Film Thickness
Page 2
2. Quantitative 2-D Fluorescence Images Obtained in a Demonstration of the Fuel Film diagnostic
Page 3

III. Statement of Problem Studied

The project funded under U.S. ARO grant DAAG055-97-1-0265 was directed toward the development and use of fluorescent diagnostics in the understanding of the heating and evaporation of droplets and sprays, the role of shear in atomization processes, and the application of fluorescent diagnostics to various aerodynamic problems. At the University of Texas at Dallas (UTD), the following fluorescent diagnostic projects were undertaken: (1) real time measurements of shear (possibly in fuel spray ligaments), (2) simultaneous determination of temperature and oxygen, (3) liquid film thickness (particularly on cylinder walls), and (4) mixing of liquids. The first three projects involved students supported under this AASERT grant, and their work will be described in the next section.

IV. Summary of Most Important Results

A. Fuel Film Thickness

A new method for real-time 2-D measurement of fuel film thickness in an engine cylinder was developed. This method will be of particular importance in the development of automotive engineering strategies for avoiding the excessive hydrocarbon emissions that currently occur during cold start.

The key idea was to find a fluorescent molecule that would be co-evaporative with the fuel. If this criterion is satisfied, then the concentration of the fluorophore will remain constant in the fuel liquid throughout the evaporation process. Assuming constant concentration of the fluorophore and constant (spatial) illumination by the laser excitation source, the intensity of the fluorescence will be proportional to the amount of light absorbed, i.e., under optically thin conditions directly proportional to the fuel film thickness. In an engine, oxygen is present and the pressure and temperature change substantially during the engine cycle, and hence the fluorophore must also be insensitive to these changes in the environment.

About 140 potential fluorophores were examined for their suitability for use in fuel film measurements. In the end, two molecules were selected: cyclohexanone and 2-methylcyclopentanone. The photophysics of these two molecules is quite similar to the photophysics of the widely used acetone and 3-pentanone molecules. The fluorescence intensity of these two molecules is virtually independent of oxygen concentration (0-5 atm

air) and temperature (20-200 C). With the (required) excitation at 308 nm (XeCl excimer laser) they should be appropriate for quantitative real-time, 2-D imaging of fuel film thickness in the range 0-1 mm.

Figure 1 shows the calibration curve for this system. It should be possible to measure fuel film thickness within ± 0.02 mm.

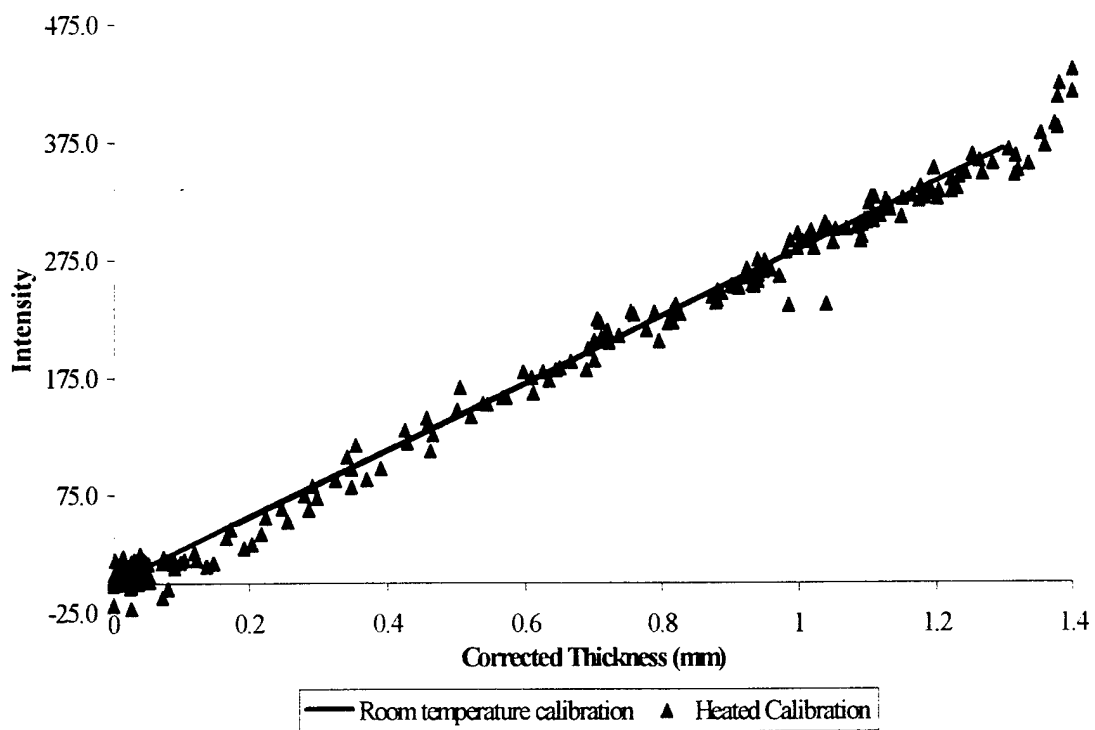


Figure 1

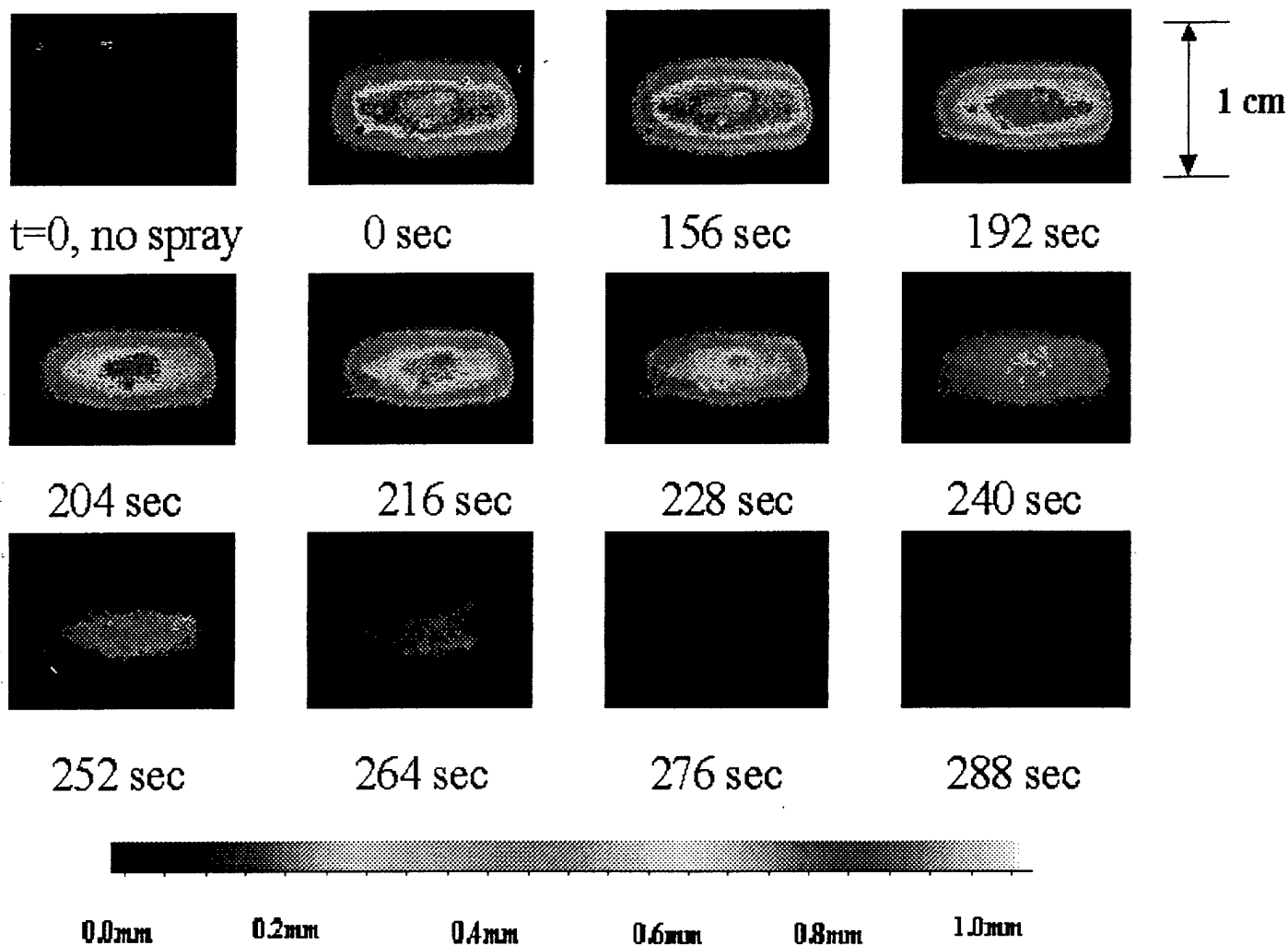


Figure 2 shows the results obtained in a demonstration experiment in which fuel (with fluorophore) was sprayed on a heated steel plate.

Jiemin Yang, now employed at Shell Chemical Company, carried out the development of the diagnostic for fuel film thickness as part of her doctoral thesis.

This work was also supported by the Ford Motor Company through their University Research Program.

B. Shear in Liquids

The process by which droplets in a fuel spray are formed from the fuel ligaments which initially emerge from a fuel spray nozzle is poorly understood. One possibility is that shear induced by the movement of the ligament through the air is the dominant mechanism and that droplets are formed where the regions of shear in the liquid are highest. A fluorescent diagnostic for shear in the liquid would be valuable in assessing such a mechanism.

In order for a fluorescent molecule to be sensitive to the levels of shear estimated for such processes ($< 10^4 \text{ sec}^{-1}$), its dimensions must be large ($\approx 1 \mu$) compared to molecular dimensions so that rotational relaxation does not dominate the modest anisotropy induced by the relative motion of two neighboring lamina in the liquid. One way to carry out such a scheme would be to use polymers that have been labeled with a fluorophore whose emission is sensitive to the polymer conformation. At low shear, the polymer should exist in a random coil conformation, and at high shear it should have a more open conformation. However, these shear-induced conformational changes are also the conformational changes that are involved in shear thinning of polymer

solutions, and introduction of shear-thinning fluorophores into a fuel spray experiment would alter the mechanism of spray formation. The high sensitivity of fluorescence measurements is the key to development of a shear sensitive diagnostic might function in spite of these conflicting requirements. If a shear sensitive polymer could be found in which the fluorescence changes as a function of shear, then perhaps it could be used at low concentrations so that shear thinning was negligible and yet the fluorescence could be measured.

The student who worked on this project, Jeanne Martino, examined numerous shear sensitive polymers, but did not find or develop a fluorescent polymer which was sensitive to shear. She left the doctoral program with the project incomplete.

Later, a collaboration with Professor Francoise Winnik at the University of Montreal emerged. We loaned her our home made device for measuring fluorescence at defined shear values, and she and her coworkers have tested their fluorescently-labeled polymers. In April 2001, they found a system that may lead to a successful fluorescent diagnostic for shear in liquids. This collaboration and its fruits will be described in more detail in the final report for U.S.ARO grant DAAG055-97-1-0265.

As part of this collaboration, Daniel Haradem, an M.S. student, carried out a literature search on shear thinning polymers and fluorescence. These papers were sent to Professor Winnik in order to aid her work.

V. List of Publications

A. Peer-Reviewed Journals

"A Fluorescence-Based Method for Quantitative Measurement of Fuel Film Thickness During Cold Start of Engines, with J. Yang, *Appl. Spectrosc.*, 54, 565-574 (2000).

C. Presentation at Meeting

"A Fluorescence-Based Method for Quantitative Measurement of Fuel Film Thickness During Cold Start of Engines, with J. Yang, Federation of Analytical Chemistry and Spectroscopy Societies, October 1-2, 1998, Austin, TX.

VI. Participating Scientific Personnel (Students supported)

Jiemin Yang, Doctor of Chemistry degree awarded, August 1998

Jeanne Martino, doctoral student, left without completing degree, December 1998

Darren Lee, doctoral student, left without completing degree, August 2000

Daniel Haradem, M.S. degree awarded, August 2000

VII. Report of Inventions

None