Solicitation Number:	ARMY RESEARCH OFFICE PROPOSAL COVER PAGE	ARO Proposal Number

1. SUBMIT 10 COPIES OF PROPOSAL TO: Director U.S. Army Research Office ATTN: AMSRL-RO-RI P.O. Box 12211 Research Triangle Park, NC 27709-2211	2. For consideration by ARO Organization Unit(s): ☐ Biology/Life Sci ☐ Materials ☒ Chemistry ☒ Mathematics ☒ Computer Science ☐ Physics ☐ Electronics ☐ Engineering ☐ Environmental Sciences	3. Is this proposal being submitted to another Federal Agency? ☒ No ☐ Yes If Yes, list the agency:
	4. Is applicant delinquent on any Federal Debt? ☐ Yes (Attach explanation) ☒ No	5. Proposal Valid Until (min of 6 mos): 09/01/2003
6. Entity Identification Number (EIN) or Taxpayer Identification Number (TIN) 416007513	7. Data Universal Numbering System (DUNS No.): 555917996	8. Commercial and Government Entity (CAGE) Code: 0355

9. Name of organization to which award should be made: University of Minnesota	10. Administrative Address of Organization (if different): 11. Branch/Campus/Other Component (where work is performed, if different):
12. Submitting Organization's Contract/Grant Administration Office: Sponsored Proj. Adm.,450 McNamara Alumni Ctr. 200 Oak St. SE, Minneapolis, MN 55455-2070	13. Submitting Organization's Audit Office:

14. Submitting Organization: (Check all that apply)
☐ For Profit: ☐ Large ☐ Small ☐ Disadvantaged ☐ 8a ☐ Women-Owned ☐ Foreign ☐ Individual
☒ Educational: ☐ HBCU ☐ Minority Institution ☐ State ☐ Private ☐ Foreign ☐ FDP
☐ Hospital: ☐ Public ☐ Private ☐ Nonprofit ☐ For Profit
☐ Nonprofit
☐ Not-For-Profit
☐ Other (Specify)

15. Check appropriate box(es) if this proposal includes any of the items listed below: ☐ Human Subjects ☐ Recombinant DNA ☐ Vertebrate Animals ☐ Genetically Engineered Organisms ☐ National Environment Policy Act ☐ Limited Rights Data ☐ Disclosure of Lobbying Activities ☐ Historical Places	16. Proposed Amount: 30,000.00 17. Proposed Duration (1-60 mos): 12 mos 18. Proposed Start Date: 09/01/2003	19. Type of Award Proposed: ☐ Single Investigator ☐ Young Investigator Program ☒ Short Term Innovation Rsch ☐ Research Instrumentation ☐ HBCU/MI ☐ Other (specify):

20. Title of Proposed Project:
Cleanup Properties of High Molecular Weight Polymeric Solutions Laden with Particles

21. Principal Investigator (PI)/Project Director (PD) Department and Postal Address:
Aerospace Engineering and Mechanics,107 Akerman Hall,110 Union St. SE, Minneapolis, MN 55455

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25 a. Authorized Representative Signing for Applicant Organization: Kevin McKoskey 25 b. Title: Grants Manager	25 c. By signing and submitting this proposal, theofferor is providing the certifications found in Part IV, Section 5. 25 d. Signature Date:

ARO Form 51 (REV Oct 98) PREVIOUS EDITIONS OF THIS FORM ARE OBSOLETE

C. *Abstract*

This project is to exploit properties of high molecular weight polymeric solutions for applications to cleanup of contaminated solid and liquid (oil slick) surfaces. Recent experiments of Wang and Joseph (2002) have shown that the addition of small solid particles to these solutions can greatly enhance the cleanup properties. The research focuses on applications, defining application areas and the operating conditions for good cleanup, and on theoretical issues directed at understanding the extensional properties of high molecular weight polymeric solutions especially when they are laden with small particles. The methods to be employed to achieve these objectives are primarily experimental; theoretical issues are to be addressed also by numerical simulation and mathematical analysis. The experimental results that motivate this proposal are innovative rather than incremental. The research requires a much larger budget than is allowed in this STIR proposal which is directed at further "proof of concept" results.

D. Project Description

The most compelling argument for this project is the series of click on movies of the experiments which can be found at http://www.aem.umn.edu/research/cleanup and is available on CD-ROM for reviewers of this proposal.

This project is associated with the remarkable properties of the tubeless siphon and particle-laden tubeless siphon which allow contaminants to be cleaned remotely by suction devices. Filaments of high molecular weight polymeric solutions can support very high extensional stresses without breaking. This allows one to siphon pools of these solutions on solid or liquid substrates remotely in a tubeless siphon. The tubeless siphon is described in standard works on rheological fluid mechanics say Bird, Armstrong and Hassager 1977, Joseph 1990 and Macosko 1994. The siphon may be described as follows: a fluid is sucked through a nozzle with the nozzle elevated above the surface of the liquid. Instead of the liquid breaking as in unthickened (Newtonian) liquids like water, glycerin or oil, an unsupported fluid column is drawn from a pool below into the nozzle above without breaking as shown in figures 1 and 2.

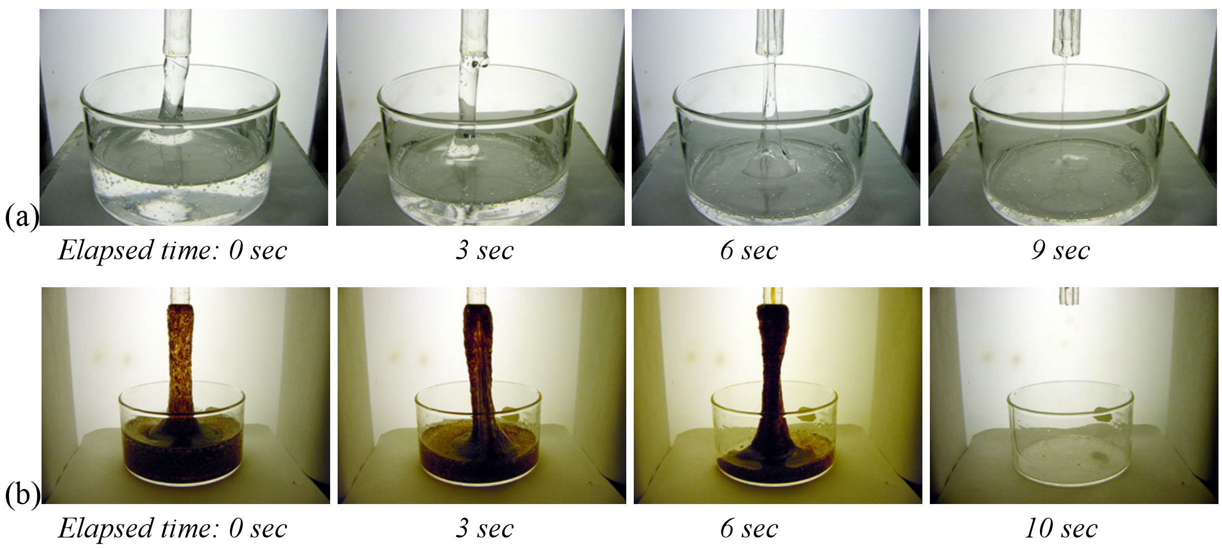

Figure 1. Sequential photos of a tubeless siphon of 1% aqueous Polyox solution, (a) With no particles, the fluid is not cleaned up. (b) With a high concentration of particles, all the fluid and particles are removed. The particles are resin particles with a size in the range of 600-700 μm.

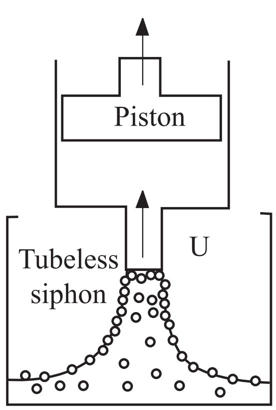

Figure 2. The schematic of the experimental set up.

The thickened (viscoelastic) liquids may be sucked from a substrate remotely with a "vacuum cleaner". It appears not to have been known before the recent work of Wang and Joseph 2002 that if the rate of withdrawal, the sucking power, is high enough or if the sucking power is much lower but the liquid loaded with small particles in concentrations less than 10%, the substrate can be cleaned completely. This very remarkable cleaning property can be seen in the movies of our experiments on our web site and in CD-ROM, which is available upon request.

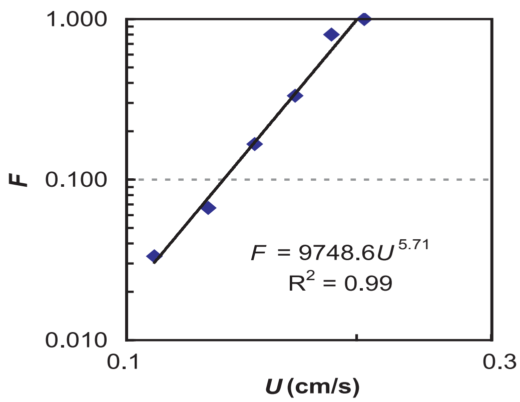

Figure 3. Suction fraction of fluid left behind as withdrawal velocity.

In the case when no particles are present, one can monitor the volume of liquid left behind after the siphon breaks as a function of the rate of suction (the velocity of the piston). The suction fraction F, defined as the volume sucked out to the initial volume, increases as 5.71 power of the velocity. At a high enough velocity one gets complete cleanup, even when no particles are present.

Similar experiments demonstrating effective cleaning by sucking off high molecular polymeric liquids were done with oil rather then water-based solvents. These experiments were motivated by the idea that if solid substrates could be cleaned by pulling off thickened liquids, preferably laden with particles, the same could be done with oil slicks. Motor oil was spread on water in a petrie dish; the oil slick could not be sucked out with a handheld piston cylinder device because the oil would break when sucked. Then STP (a weakly polymeric liquid) was put on top of the motor oil and the two oils mixed. The STP-oil slick mixture could be pulled off the water easily under the same conditions that the oil alone could not be. The patent office at the University of Minnesota searched for and found a patent which had evolved to a product *Elastol*; this is a high molecular weight polymer which may be mixed with oil for oil slick removal. Elastol is in liquid and powder form. The Elastol people do not yet know that their product could be used for cleaning solid substrates and the beneficial effects of adding particles as described below.

Three experiments were done and can be seen at our web site or on a CD-ROM (contact *dvogel@aem.umn.edu* or see *http://www.aem.umn.edu/research/cleanup*).

1. Cleaning of solid substrates covered with oil by adding small amounts of Elastol with better cleaning when small particles are added to the oil-Elastol mixture.
2. Improved cleaning oil-slicks by adding particles to the oil-Elastol mixture.
3. Capillary attraction and self-assembly of small particles in oil slicks

These experiments will now be described with words and pictures, but they are much better described with the movies.

1. Cleaning oil contaminated solid substrate with Elastol and Elastol-plus particles.

A handheld piston with a cylinder-sucking device is used to demonstrate the principles. There are five parts.

i. Oil is in the beaker and it cannot be sucked out.

ii. A small amount of Elastol is added to the oil (say 5%).

iii. The oil plus Elastol can be pulled out but the bottom of the beaker is slightly soiled with oil.

iv. Particles are added to the oil-plus-Elastol. The particles are sub-millimeter and nearly neutrally buoyant. The particles are not special, they are polydisperse and not spheres.

v. The Elastol-oil-particle mixture is pulled out of the beaker; the bottom of the beaker is cleaned.

i.

iii.

v.

Figure 4. Cleaning oil with Elastol and Elastol plus particles.

2. Oil spill remediation.

i. Motor oil on water in a petri dish forms an oil slick.

ii. It cannot be sucked off because the oil breaks.

iii. A small amount of Elastol is added and mixes with the oil.

iv. The mixture can be sucked off, but a little slick is left.

v. particles are added. The mixture cleans up nicely, better than with no particles.

ii.

iv.

v.

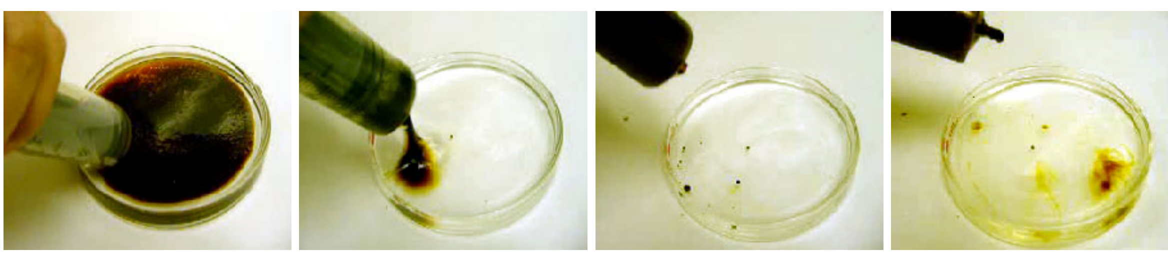

Figure 5. Oil spill remediation.

3. Capillary attraction and self-assembly of small particles in oil slicks.

Heavy hydrophobic particles will float on water. They are held up by capillary forces at the contact line. When small particles are placed in an oil slick, they are covered with oil and are even more hydrophobic.

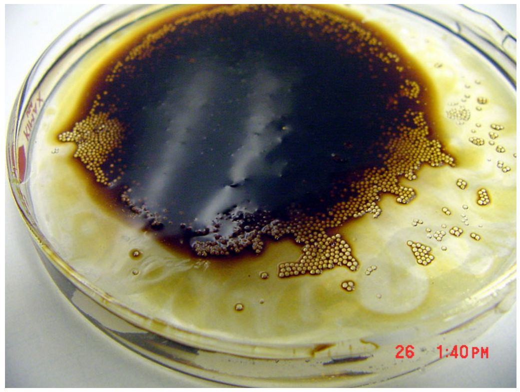

Figure 6. Capillary attraction of small particles in an oil-Elastol mixture.

A comprehensive review of self-assembly due to capillarity can be found in the paper by Joseph, Wang, Bai, Yang and Hu, 2002. which has been submitted for publication and can be downloaded from *http://www.aem.umn.edu/people/faculty/joseph/archive/docs/capillarity.pdf*. The floating particles used so far in the experiments are chemically passive. The use of active particles for remediation and decontamination have as yet to be studied.

Proposed research and homeland defense

The proposed research focuses on homeland security and on scientific issues which are implied by experiments just described. The applications are to cleanup and disposal of solid and contaminated substrates. One could imagine covering a contaminated solid, a portion of an airplane or tanks, with a thickened liquid laden with particles, then sucking off the liquid, particles and contaminant remotely with a powerful vacuum cleaner newly designed for efficient removal and disposal.

The removal of particle-laden thickened liquids may be regarded as a competitor for foams say in Anthrax applications. If such a liquid is laid on an anthrax contaminated surface, there is no way that the spores could be aerosolized. Moreover, it is likely that the spores would be trapped in the thickened liquid and sucked away with the liquid for safe disposal.

The efficient removal of oil slicks is another application, possibly more related to environmental protection than to homeland defense.

Research projects

The research maybe divided, but not strictly, into applications and science. The application studies focus on how fluid, particles and apparatus parameters can be adjusted for optimal cleaning.

Solution properties

The molecular weight, type and concentration of the polymer and the quality of solvent-polymer interactions will be varied and evaluated for optimal cleaning.

Particle properties

These studies aim to evaluate the effects of size, weight, concentration, wetting and reactivity properties on cleanup. What are the optimal weights and concentrations? nano-particles?

Sucking apparatus properties

Since the cleaning property of siphon depends on the rate of withdrawal and since many requirements for effective manipulation, placement, storage and disposal will inevitably arise, the design of effective sucking devices ought to be studies and implemented. Excellent results were achieved in our experiments using only a handheld piston and cylinder device. Very great improvements in cleaning can be expected from a well-designed device pointing to spreading, removal and disposal of particle-laden polymeric solutions on and from contaminated substrates.

The ***direct sciences issues*** of this research focus on understanding of particle-laden tubeless siphons under realistic conditions. The role of particles in enhancing extensional stresses is a virgin subject without prior art. The study of these topics requires understanding at a fundamental level of the mathematical modeling of viscoelastic and multiphase flow; Joseph is an expert in these two topics. Theoretical studies will be undertaken on…

1. Spreading dynamics. In the vision for this kind of cleanup it would be necessary to first spread the particle-laden polymeric liquid on a contaminated substrate. Studies of spreading of viscoelastic liquids should be considered.
2. Fluid dynamics of tubeless siphons without and with particles. All of the mathematical analyses of tubeless siphons are based on idealized extensional flows which are far from reality. There is nothing in the literature on the effects of small particles on extensional flows other than the paper of Wang and Joseph 2002.
3. The experiments cited in this proposal demonstrate that soiled beakers may be cleaned remotely by sucking off the polymeric liquid at high rates of withdrawal. The study of rate effects on substrates which are not beakers needs to be understood.

The complicated problems just described are best studied by numerical methods which have been developed at Minnesota and elsewhere in successive Grand Challenge and KDI-NSF grants to D.D. Joseph, PI.

STIR Proposal

This proposal for innovative research is regarded as a “proof of concept” effort. In fact the concept and supporting evidence has been laid down here. The work which we would do with $30,000 is to extend the cleanup experiments to even more contaminated surfaces focussing first on dirty rough and pitted surfaces.

Relevance of this research to Army interests

This research is relevant to the decontamination and safe disposal of toxic materials. The possibilities presented by particles in mixtures of polymeric liquids and particles for catalytic reaction and active chemistry have not been done and are of interest in research Area I (chemistry) of Dr. Stephen Lee. The fluid mechanics aspects of the tubeless siphon and solid laden polymeric liquids, together with the possibilities for creating “smart” liquid-laden materials falls unto research Area II of Dr. John Lavery. The fluid mechanics problem is very challenging and requires skills in applied analysis and physical mathematics. The most interesting theoretical challenge posed by our experiments is the enhancement of the pulling power of the particle-laden tubeless siphons. The role of particles in the enhancement of extensional stresses is a virgin subject without a prior art. These are complicated problems of a kind described by Joseph (2000) which are best described by numerical methods. D.D. Joseph was the PI of an interdisciplinary program on direct numerical simulation of solid liquid flow funded successively by the NSF first as a Grand Challenge and then as a KDI grant. Singh and Joseph (2002) have developed a hybrid distributed LaGrange multiplier method for solids in fluids together with level set methods for free surface problems; they use this package to analyze the self assembly due to capillary attraction of floating particles. This aspect of the proposed project fits the parameters of described research interests in computational mathematics of Dr. Stephen Davis.

E. Biographical Sketch

Daniel D. Joseph has been a Professor at the University of Minnesota for 40 years and a Regents Professor since 1991. He is a member of the National Academy of Sciences, National Academy of Engineering, American Academy of Arts and Sciences. He holds the Bingham Medal of the Society of Rheology, the Timoshenko Medal of the ASME, Fluid Dynamics Prize of the APS, the G.I. Taylor Medal of the Society of Engineering Science, and numerous academic, industrial, and visiting lecturer honors. He is listed in the ISI's Highly Cited Researchers. He has 10 patents, has written 5 books and edited 4, has served as editor of more than 12 academic journals, and published over 300 articles.

Professor Joseph has had a long association with Army funding agencies. He has been supported by ARO mathematics for over 20 years. He received the CRDEC Distinguished Service Award in 1992 for his contribution toward evolving a means of eliminating projectile flight instabilities produced by viscous liquid-fills. He has worked and is working on problems of aerodynamic dissemination for missile defense with contacts in SDC, BMDO and MDA.