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EVALUATION OF ANTI-FREEZE VISCOSITY MODIFIER FOR POTENTIAL EXTERNAL TANK APPLICATIONS

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16. ABSTRACT

Viscosity modifiers and gelling agents have been evaluated in combination with ethylene glycol and dimethyl sulfoxide water eutectics. Pectin and agarose were found to gel these eutectics effectively in low concentration, but the anti-freeze protection afforded by these compositions was found to be marginal in simulations of the intended applications. Oxygen vent shutters and vertical metallic surfaces were simulated, with water supplied as a spray, dropwise, and by condensation from the air.

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Samples of pectin were provided by Mr. Terry Schneider of Rockwell International, Downey, California, who was also most helpful in giving background information concerning experimentation performed at his location.

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INTRODUCTION

The Space Shuttle External Tank (ET) has several areas which are subject to ice/frost formation. These consist of protrusions which are not covered by thermal protection, and louvers in the oxygen vent system (Fig. 1). While frost formation is relatively harmless, thick accumulations of ice on the Shuttle side of the ET can present hazards to the Shuttle's thermally protective tiles.

Various proposals have been made to prevent or eliminate such ice formations, including the use of hot gases or anti-freeze liquids. The hot gas concept requires large capital outlays and presents the potential hazards associated with the use of large volumes of uncontained oxygen-poor atmospheres. The anti-freeze liquids tend to be highly fugitive, draining away rapidly. To counter this latter drawback, Rockwell International proposed the use of a gelling agent, specifically the pectin/dimethyl sulfoxide (DMSO) combination.

This present work has undertaken to evaluate this proposal and the overall general concept. It was decided to limit the anti-freeze liquids to DMSO, as chosen by Rockwell, and the commonly used ethylene glycol. A list of thickening/gelling agents was drawn up, but not all were evaluated, for reasons of availability, relative complexity, etc.

EXPERIMENTAL

De-Icers

1) Dimethyl sulfoxide
2) Ethylene glycol.

Viscosity Modifiers

1) Acrylamide
2) Agarose
3) Gelatin
4) Gum tragacanth
5) Hydroxy methyl cellulose
6) Pectin
7) Sodium alginate
8) Starch.

Solution Preparation

Generally, solutions were prepared in 50 ml quantities, using a magnetic stirrer and heating to 102° to 104°C. The thickener was dispersed in the de-icer prior to addition of the water and application of heat. Solutions were allowed to cool without agitation. In the preparation of "micro-gels," solutions were prepared as above in 100 ml quantities, followed by cooling with vigorous stirring. Agitation was provided by a split-disc type propeller, using speeds sufficient to maintain a vortex.

Solution Properties

1) Acrylamide was not tested since gel-formers were found which were simpler than this precise three component system.

2) Gelatin appeared to have limited solubility and formed only gelatinous inhomogeneities.

3) Gum tragacanth increased the viscosity of the eutectics and could be useful at higher concentrations. Insoluble components were noted in accordance with literature notations.

4) Sodium alginate and hydroxy methyl cellulose were not evaluated for reasons of timing and availability.

5) Starch was not effective at the 2 percent level.

6) Agarose powder (Bio-Rad Laboratories, Richmond, California) was found to be an excellent gel-former. Gels may be destroyed by heating and do not re-form upon subsequent cooling. "Micro-gels" having a paste-like consistency may be formed by cooling with vigorous agitation. An endotherm was noted in the 12° to 14°C range while cooling with ice to form these microgels. These gels and microgels do not dissolve readily in water and do not tend to completely dry out upon exposure to the room atmosphere for several days. Gel firmness is dependent upon agarose concentration.

7) Citrus pectin (Atlantic Gelatin, General Foods Corporation, Hollywood, California) produced gels as reported by Rockwell International. Powder solubilities appeared to be somewhat lower than those with agarose, but the gels were more water-soluble. Gel-forming minimum concentrations were greater than with agarose, and gel formation occurred over a broad temperature band during the cooling process. Micro-gels could not be formed with the agitation employed, but rather, large gel particles were produced.

Evaluation of Gel Anti-Freeze Properties

Evaluations were conducted on the vertical sides of a steel beaker, copper piping, and a louver simulation.

1) The louver simulation consisted of 11/16 in. wide aluminum strips embedded at 45° angles in one end of a 2 in. I.D. cork cylinder. with 1/4 in. spacing between strips. This construction was attached to a 3 in. pipe from a liquid nitrogen storage vessel. Gaseous nitrogen was periodically vented through these louvers at high flow rates. Figure 2 shows this set-up, without the gels applied.

Gels applied to these metal "louvers" adhered reasonably well to the upper surface, but were blown off the underside. Micro-gels could be applied more easily and evenly, but were also blown off the bottom surface. Ethylene glycol gels tended to be harder and flake off more readily than did DMSO gels. When stored inside, the gels lasted for about a week before the liquid components evaporated. Rain washed away the gels.

No frost formation was noted on gel coated surfaces under conditions of the tests.

2) For simulation of uninsulated tank hardware, the vertical sides of a two-liter steel beaker were used. Liquid nitrogen was passed through cooling coils submerged in ethanol to cool the beaker. Temperature measurements were made with a thermocouple immersed in the circulating ethanol. Temperatures as low as -93°C were obtained. Gels were applied to the side of the beaker with a spatula. Water was supplied either as moisture condensation from the air, in the form of a fine spray from a gun, or in a stream from a squeeze bottle. Considerable difficulty was experienced in getting normal gels to cling to the beaker sides, and an even coating was impossible. Dispersion of the gels in gum tragacanth solution improved the adherence but the gel lumps still caused uneven coating. Microgel pastes could be applied smoothly and evenly and adhered well.

For the controlled thickness experiments, cardboard was taped to the beaker sides to form a well, which was filled with the microgels. In all cases, gels were applied at room temperature and then cooling was begun.

Thin Coatings (ca. 50 mils)

a) DMSO (60/40) with pectin frosted over by the time the bath was cooled to -62°C and water rivulets froze on the surface when applied at -82°C. A 50:50 mixture of this material and the DMSO 70/30 agarose microgel gave the same results. The pectin microgel does not adhere significantly better than the normal gel.

b) DMSO (70/30) agarose microgel frosted over very slightly but slower than the combinations above. When sprayed with a water mist at -46°C, a hard ice coating formed over the pliable gel substrate.

c) Ethylene glycol (75/25) agarose microgel results were similar to those in b), with a slightly stiffer gel substrate.

Thicker Coatings

Ethylene glycol (75/25) agarose microgel:

a) 100 mils frosted at -51°C

b) 200 mils frosted at -93°C

c) 300 mils no frost at -93°C.

All coatings shrink drastically at -93°C, recover at room temperature but tend to "mud-crack" upon recovery. Some liquid loss probably occurred during the overnight warming process.

3) In an attempt to evaluate temperatures closer to -185°C, gels were applied to copper piping leading from the LN_2 dewar. Temperature was measured by means of a thermocouple at the pipe surface below the gel. Temperatures as low as -166°C were attained.

a) The ethylene glycol (75/25) agarose microgel in 400 mil thickness formed a light frost at -140°C, and a heavy frost at -166°C. A drop of water placed on this surface froze immediately but the gel was pliable underneath down to the pipe surface.

b) DMSO (60/40) pectin gel in 600 mil thickness formed heavy frost at -148°C and also froze a drop of water placed on the surface. The gel remained flexible.

Both the glycol microgel and DMSO gel formed brittle solids when plunged into liquid nitrogen. When warmed to room temperature, no differences were detected compared to the original gels.

DISCUSSION

While the Rockwell International work was done using a 50 percent (volume) solution of DMSO in water, much of this work was done at the higher end of the eutectic range. This was done based upon the premise that water contacting the surface will dilute the interface. In test configurations, no differences in effectiveness were detected.

DMSO appears to be relatively more flammable than ethylene glycol, and the gels also appear to burn more readily. Both gels extinguish when the flame is removed and, indeed, drips from the glycol tended to extinguish the applied flame. Although the vapor pressure of DMSO is relatively low at room temperature, exposed gels give rise to somewhat noxious odors.

Caution must be used in working with DMSO due to its well known solvating power and ability to permeate human skin. Thus, while not particularly toxic itself, it could solvate some available toxins and facilitate their entry into the human body.

CONCLUSIONS

1) Microgels, having a paste-like consistency, can be more effectively applied to vertical surfaces than can conventional gels. These could be formed readily with agarose, but not with pectin.

2) Ethylene glycol is preferred to DMSO for reasons of reduced flammability, health hazard potential, lower evaporation rate, and broader eutectic range.

3) Gelled antifreeze is effective for substrate surface temperatures in the -18°C range, but ineffective for -184°C substrate temperatures when used in "reasonable" thicknesses. It is highly probable that the insulating properties of the gels contribute more to their effectiveness than does the formation of an eutectic with added water.

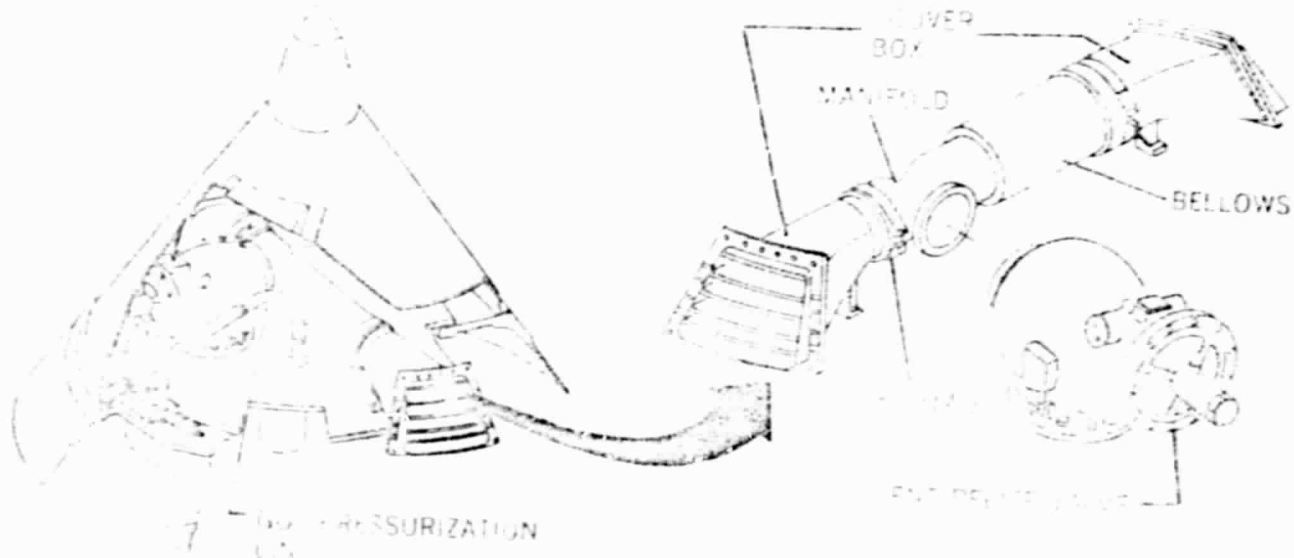
4) Pectin gels are readily dissolved by liquid water, unlike agarose gels. In theory, pectin should be more effective in the prevention of ice or ice/frost formation. In practice, at cryogenic substrate temperatures, the gel surface itself is cold enough to form ice before any solvation can occur.

TABLE 1. SELECTED PHYSICAL PROPERTIES COMPARISON

	Ethylene Glycol	Dimethyl Sulfoxide
Molecular Weight	62.07	78.13
Boiling Point (760 mm Hg, °C)	197.6	189.0
Vapor Pressure (20°C, mm Hg)	0.06	0.417
Freezing Point (°C)	-13	18
Density (20°C, g/cc)	1.11	1.10
Viscosity (20°C, cp)	20.9	2.47
Surface Tension (20°C, dynes/cm)	48.4	46.2
Coefficient of Expansion (20°C, cm^3/°C)	6.2×10^{-4}	8.8×10^{-4}
Flash Point		95°C
Spontaneous Ignition Temperature in Air	480°C	301°C
Heat of Combustion	-283.3 kcal/mol @20°C	-472.9 kcal/mol @25°C
Range of Eutectic (wt.%)	58-80	55-70

TABLE 2. SOLUTION PROPERTIES

De-Icer	V/V De-Icer/H_2O	Thickener Grams/100 ml Solution	Solution Properties
Quiescent Cooling			
DMSO	60/40	Starch:2	Little viscosity increase down to -15°C, clear soln.
Glycol	60/40	Starch:2	Slight viscosity increase down to -15°C, white ppt.
DMSO	60/40	Gelatin:2	Little visc. inc. r.t., incipient gel at -15°C, white ppt.
Glycol	60/40	Gelatin:2	Little visc. inc. r.t., incipient gel at -15°C.
DMSO	60/40	Gum Trag:2	Some visc. inc. r.t., viscous cold, some particulates
Glycol	60/40	Gum Trag:2	Some visc. inc. r.t., viscous cold, some particulates
DMSO	60/40	Agarose:2	Gel at room temperature, slightly cloudy
Glycol	60/40	Agarose:2	Gel at room temperature, slightly cloudy
DMSO	60/40	Agarose:1	Gel at room temperature, slightly less cloudy
DMSO	70/30	Pectin:2	Heat to 85°C, gell with undissolved particles
DMSO	50/50	Pectin:1.4	Heat to 85°C, good gel at r.t.
DMSO	50/50	Pectin:2	Heat to 85°C, good gel at r.t.
Glycol	50/50	Pectin:2	Heat to 85°C, good gel at r.t.
Gel Formation Under Agitation			
DMSO	70/30	Agarose:2	Smooth paste, maximum gellation ca. 14°C.
Glycol	75/25	Agarose:2	Smooth paste, maximum gellation ca. 12°C.
DMSO	60/40	Pectin:2	Large gel particles formed from 49°C to 25°C.
DMSO	70/30	Pectin:1	104°C before solution, only dispersed gel particles.
Glycol	75/25	Pectin:1	Good gel 13.1°C, solubility better than with DMSO.
Glycol	75/25	Agarose:0.5	Only dispersed gel particles.



*Reproduced from "System Definition Handbook, Space Shuttle External Tank," MMC-ET-SE25-0, DR SE25 WBS 1.6.2.2. NASA-30300

Figure 1. ET GO_2 vent/relief valve and manifold.

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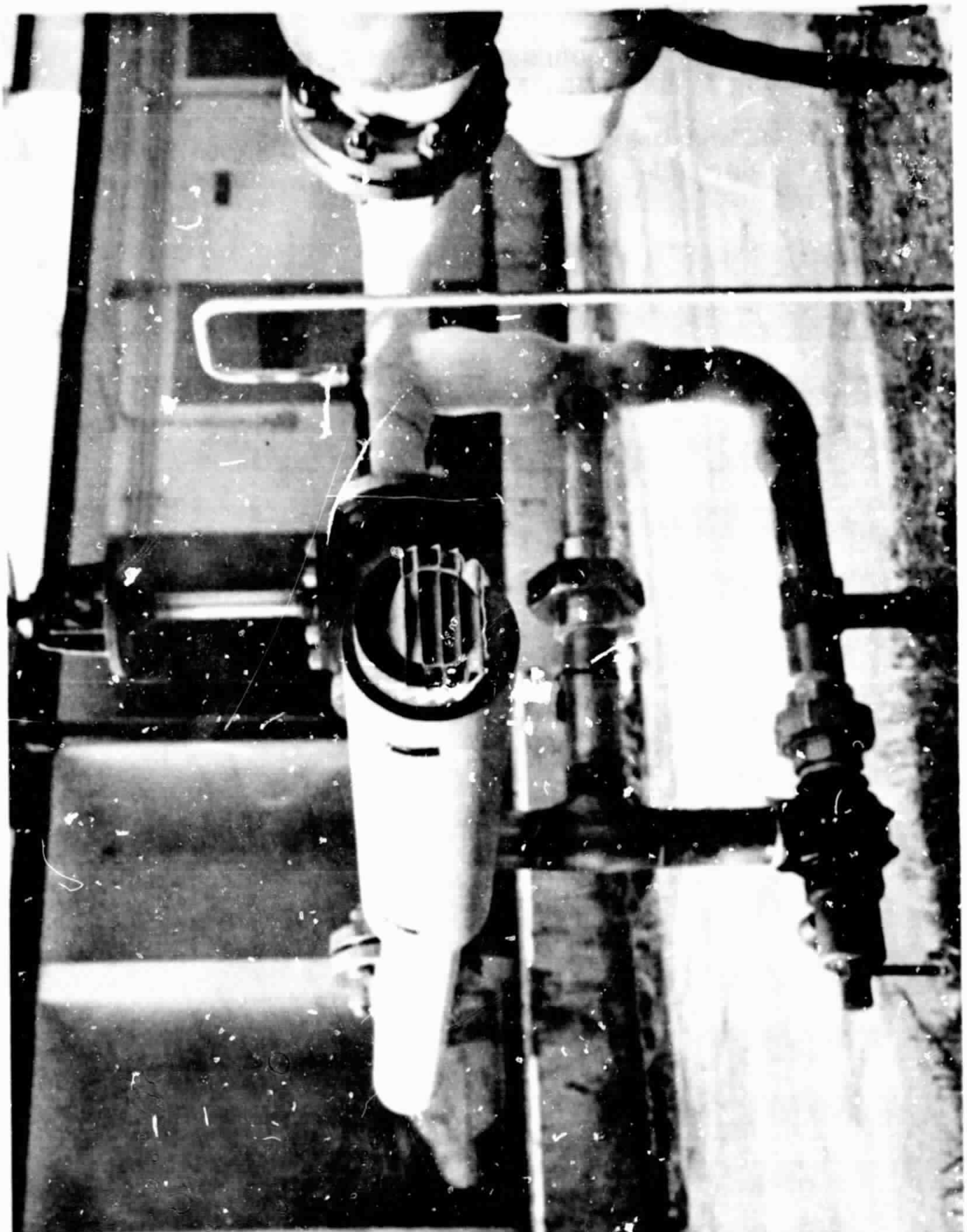

Figure 2. ET relief louver simulation.

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APPROVAL

EVALUATION OF ANTI-FREEZE VISCOSITY MODIFIERS FOR POTENTIAL EXTERNAL TANK APPLICATIONS

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The information in this report has been reviewed for technical content Review of any information concerning Department of Defense or nuclear energy activities or programs has been made by the MSFC Security Classification Offices. This report, in its entirety, has been determined to be unclassified.

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