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THIXOTROPIC PROPELLANTS AND UNIT OPERATIONS

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THIXOTROPIC PROPELLANTS AND UNIT OPERATIONS

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NOTICE

ABSTRACT

A program was established to set up unit operations in organic chemistry for use in support of contract and company sponsored research. In addition, an experimental program was conducted to determine the feasibility of gelling liquid propellants which would exhibit thixotropic properties. Propellants under consideration were: 50/50 fuel blend, hydrazine, UDMH and N_2O_4.

CONTENTS

ILLUSTRATIONS

Figure | Page

TABLES

I. SUMMARY

This report covers work originally planned in the field of Unit Operations plus work done as a cooperative effort with the Research Department. The latter was an experimental program conducted to determine the feasibility of forming lyophilic sols, which would exhibit thixotropic properties, using certain selected high energy gelling agents with 50/50 fuel blend, hydrazine, UDMH, and N_2O_4. Compatibility tests were performed between the various gelling agents and propellants, followed by attempts to form thixotropic gels with suitable candidate materials. The measurement of physical properties was then undertaken on the thixotropics which were formed.

II. INTRODUCTION

A program was established to set up unit operations in organic chemistry for use in support of contract and company sponsored research. In addition, an experimental program was conducted to determine the feasibility of gelling liquid propellants which would exhibit thixotropic properties. Propellants under consideration were: 50/50 fuel blend, hydrazine, UDMH and N_2O_4.

III. PROCEDURES

A. FABRICATION OF THIXOTROPIC GELS

The following three methods were used in forming gels for this program:

(1) Hand Mix – Tared quantities of gelling agents and fuel are placed in a 500 ml large mouth stoppered bottle and shaken by hand until mixture is uniform.

(2) Regular Mix – Gelling agent is placed in a closed mixing kettle equipped with a power agitator. Fuel is added and the mixture is agitated for 15 minutes. At this point, the gel is forced out of the kettle through a stopcock in its base by application of pressurized nitrogen.

(3) Vacuum Mix – Gelling agent is placed in a closed mixing kettle and vacuum is applied to the system for 15 minutes. The system is isolated under vacuum and the fuel is metered in and agitated for two minutes under its own vapor pressure. At this point, the gel is forced out of the kettle through a stopcock in the base by application of pressurized nitrogen.

B. COMPATIBILITY TESTS FOR GELLING AGENTS

(1) Spot Tests – A small quantity of gelling agent is placed on a standard spot plate and several drops of fuel or oxidizer are carefully added. The mixture is visually observed and rejected if any violent reaction is noted.

(2) 24 Hour Tests – Any candidate materials which pass the spot test are subjected to a 24-hour compatibility test. To 4 cc of the fuel or oxidizer being tested is added 3% by weight of the gelling agent. The container is sealed and equipped with a pressure manometer

containing a 1-inch column of mercury in the case of fuels or fluorolube in the case of oxidizers. A room temperature water bath is used for fuels, while the N_2O_4 oxidizer is maintained at 5°C. If sufficient gas pressure is generated over 24 hours to blow out the mercury or fluorolube column, the materials fail to pass the 24-hour compatibility test.

C. VISCOSITY MEASUREMENT OF THIXOTROPIC GELS

Since viscosity is the simplest method for measuring thixotropic breakdown, emphasis was placed on developing techniques for making this measurement. Accordingly, high shear viscometers were obtained from the Cannon Instrument Company for this purpose. A pressurizing system containing a ballast tank in line to smooth out fluctuations was fabricated and set up with the high shear viscometer (Figures 1 and 2).

Preliminary attempts to determine the viscosity of prepared gel formulations using this system were found to give erroneous results. This was due to the channeling effect of the pressurizing gases. To prevent this, a baffle plate was installed in the viscometer, and additional measurements were made. These showed that the baffle plate relieved the channeling effect, but additional measurements are necessary to determine the effect of the baffle plate on the viscometer constant. Standards for calibrating the viscometer were ordered for this purpose, but not received.

Results of the above tests were inconclusive and are not included in this report.

Figure 1. High Shear Viscometer

Figure 2. High Shear Viscometer

IV. DISCUSSION AND RESULTS

A. UNIT OPERATIONS

A Todd Fractionating Column was set up at 3C-BTC. Hydrazine and UDMH were fractionated under vacuum yielding high purity materials. A total of 1,268 grams of high purity UDMH was obtained. The fraction taken had a boiling point of 62°C at 743.1 mm of Hg. A total of 2,322 grams of high purity hydrazine was also obtained and had a boiling point of 61°C at 13mm Hg. Facilities were also acquired to permit vacuum and forced air drying and they were used on the thixotropic program. Grinding and blending equipment was installed and used in the preparation of solid propellants. Unit operations for filtration, extraction purification, crystallization and refluxing were set up and used in the preparation of starting materials for solid propellant work.

B. THIXOTROPIC GELS

Spot test compatibilities were conducted between all selected gelling agents and 50/50 fuel blend and hydrazine before any appreciable quantities were mixed. Nitrocellulose was found to be reactive with both fuels and was rejected as a candidate gelling agent.

The remaining gelling agents were then further checked for compatibility with the fuels by mixing them at ambient temperature in a closed system which was equipped with a manometer for measuring pressure build-up. In no case, after standing for a 24-hour period, was there any evidence of noticeable pressure build-up or chemical instability.

Following the compatibility tests, various proportions of the gelling agents and fuels were blended to determine whether or not a thixotropic mixture could be formed. Table I summarizes the results of this work.

Testing of N_2O_4 with various candidate gelling agents was restricted to spot tests and 24-hour compatibility tests at 5°C. No work was done on the formation of thixotropic mixtures. The following gelling agents were checked and found compatible with N_2O_4 over a 24 hour period:

Guar Gum	Aluminum Metal
Jaguar 315	Aluminum Laurate
Methocel MC	Aluminum Stearate
Methocel DG	Lithium Stearate
Methocel 90 HG	XP 1115 Polyamide
Methocel 60 HG	Barium Oxide
Methocel 70 HG	Calcium Oxide
Boron Metal	Diatomaceous Earth

TABLE I

THIXOTROPIC GELS WITH 50/50 FUEL BLEND, HYDRAZINE AND UDMH

50/50 Blend	Gelling Agent	Additive	Remarks
	Cab-O-Sil		
94%	6%	-	Weak to good Range 6 to 7% Cab-O-Sil
93%	7%	-	Good
		PVP	
94%	-	6%	No gel-soluble
		Molecular Sieve	
94%	-	6% (5A)	No gel-settles out
94%	-	6% (4A)	No gel-settles out
		Zr (OH)Cl	
94%	-	6%	No gel-settles out
		Witco No. 912	PPT
94%	-	6%	PPT
94%	-	6% No. 918	No gel-soluble

TABLE I (CONT)

50/50 Blend	Gelling Agent	Additive	Remarks
94%	-	Alumagel 6%	No gel-settles out
94%	-	Sodium 6% Stearate	No gel-settles out
94%	-	Sodium Hydroxy Stearate 6%	No gel-settles out
94%	-	Jaguar 315 cm 6%	Gel-two phases same results with Jaguar 315 FC
90%	Li Stearate 10%	-	Gel (like whip cream) large volume increase - some 50/50 settles out
90%	Al Stearate 10%	-	No gel
90%	Plexiglas 10%	-	Soluble viscous liquid
	*Methocel		
94%	6% DG	-	Viscous liquid
94%	6% DG	H O	Very viscous
94%	6% MC		Viscous liquid
94%	6% 60 HG		Viscous liquid
94%	6% 70 HG		Viscous liquid
	Polyamide X1115		
94%	6%	-	No gel - not soluble
94%	6%	C H	Two phases
	PVA		
94%	6%	-	Settles out
94%	PVC	-	Settles out
	Acetylene Black (Degassed)		
96%	4%	-	Fluid gel Range 4 to 5% A.B.
95%	5%	-	Good gel
94%	6%	-	Good gel

TABLE I (CONT)

50/50 Blend	Gelling Agent	Additive	Remarks
		Fisher Aluminum Powder, 25 to 30 Micron	
90%	-	10%	Al settles out
70%	-	30%	Al settles out
50%	-	50%	Al settles out
	Cab-O-Sil		
66%	4%	30%	Good gel
89.5%	0.5%	10%	Al suspended
	Acetylene Black		
66%	4%	30%	Good gel

N_2H_4	Gelling Agent	Additive	Remarks
	Cab-O-Sil		
95%	5%		No gel
93%	7%		Will gel - not stable
90%	10%		Will gel - not stable
85%	15%		Will gel - stable to stiff mix
		EDTA	
95%	4%	1%	No gel-Both EDTA and benzilic will form gels at higher % addition
		Benzilic Acid	
95%	4%	1%	No gel
		NH_4OH (30% NH_3)	
93%	6%	1%	No gel
		H_2O	
95%	6%	1%	No gel
	Cab-O-Sil	CH_3OH	
93%	6%	1%	No gel CH_3OH and Cab-O-Sil will gel

TABLE I (CONT)

N_2H_4	Gelling Agent	Additive	Remarks
		Octylamine	
93%	6%	1%	No gel Octylamine will promote gel with alcohol
		Ethylamino Propylamine	
93%	6%	1%	No gel
		Cheelox B-13*	
95%	4%	1%	Fluid gel Range 6 to 7% Cab-O-Sil
94%	4%	2%	Fluid gel 0.5 to 1% Cheelox B-13
93%	6%	1%	Weak gel Alkaline liquid
		Gafac*	
93%	6%	1%	No gel
		Diazopon*	
93%	6%	1%	No gel
		Witco No. 912	
93%	6%	1%	No gel
94%	-	6%	No gel thickening effect
		Witco No. 918	
94%	-	6%	No gel soluble
		Jaquar 315 CM	
94%		6%	No gel
		Jaquar 315 FC	
94%		6%	No gel
	Acetylene Black (degassed)		
96%	4%		Weak gel A.B. gels are very weak to sensitive to shear
95%	5%		good gel literature quotes 4 to 5% good gel A.B.
94%	6%		
		Cafoc RM 710*	
95%	4%	1%	Weak gel these mixes will be evaluated by viscosity measurements

TABLE I (CONT)

N_2H_4	Gelling Agent	Additive	Remarks
		Diazopon*	
95%	4%	1%	Weak gel
		PVP	
95%	4%	1%	Weak gel
		Cheelox B-13*	
95%	4%	1%	Weak gel

* Surfactant

N_2H_4	Aluminum Powder	Gelling Agent	Additive	Remarks
	Reynold 400	Cab-O-Sil	Cheelox B-13*	
65.1%	30%	4.2%	0.7%	Weak gel
70%	30%	-	-	Al settles out Mixed with turbine blade stirrer at highest RPM for minutes
			Cheelox B-13*	
68%	30%	-	2%	Al settles out
64%	30%	-	4%	Al settles out
	Reynold 1-131			
70%	30%	-	-	Al settles out
50%	50%	-	-	Al settles out

* Surfactant

UDMH	Gelling Agent	Additive	Remarks	
	Cab-O-Sil			
95%	5%	-	Fluid gel	
94%	6%	-	Weak gel	Range 6 to 7%
93%	7%	-	Good gel	Cab-O-Sil
95%	5%	Distilled UDMH	Fluid gel	Range 6 to 7%
94%	6%	Distilled UDMH	Weak gel	Cab-O-Sil
93%	7%	Distilled UDMH	Good gel	

TABLE I (CONT)

UDMH	Gelling Agent	Additive		Remarks
95%	5% (N) degassed	Distilled UDMH	Fluid gel	Range 6 to 7% Cab-O-Sil
94%	6%	Distilled UDMH	Weak gel	
93%	7%	Distilled UDMH	Good gel	
95%	5% (NH) degassed	Distilled UDMH	Fluid gel	Range 6 to 7% Cab-O-Sil
94%	6%	Distilled UDMH	Weak gel	
93%	7%	Distilled UDMH	Good gel	

V. CONCLUSIONS

(1) Metal particles larger than 5 microns will not form gels or remain in suspension with weight percent additions up to 50 percent.

(2) The addition of 2 percent of certain gelling agents will form a suspension with metal additives, while 3 to 4 percent will form a gel with fuel containing 30 percent aluminum powder.

(3) Vacuum mixing during gelation removes absorbed gases and promotes void free gels.

(4) Surfactants and wetting agents have very little effect on improving the formation of gels.

(5) Good thixotropic agents seem to be those which are insoluble in fuel, of very small particule size, and high bulk density. Typical of this are silica flour and acetylene black.

(6) Materials which are soluble in fuel do not seem to form thixotropic gels, but rather a viscous liquid which will flow. Methyl cellulose, plexiglas, and guar gum, are typical of this category.

VI. RECOMMENDATIONS

(1) Determine the minimum quantities of gelling agents required to form thixotropic fuel gels as a function of the size and shape of additive metal particles.

(2) Improve and perfect methods for vacuum mixing gelled propellants.

(3) Initiate a gelling program with oxidizers based on the experience gained on this program.

(4) Conduct further work on forming thixotropic mixtures with high energy gelling agents or gelling agents which will not degrade the energy level of the propellants being used.