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Many pyrotechnics contain valuable resources which could be used in commercial applications, for example metals (e.g. magnesium, aluminum); metallic salts of copper, strontium, and barium; oxidizer (e.g. sodium nitrate, potassium perchlorate); binders such as viton, and dyes which have reclaimed value. The Navy is seeking technology that can recover the valuable ingredients from pyrotechnic flares and smoke munitions in an environmentally acceptable manner. This Phase I program studied the recovery of constituents from a Magnesium-Teflon-Viton (MTV) pyrotechnic material. The use of near critical liquid and supercritical carbon dioxide with acetone cosolvent to dissolve the Viton-A binder component was investigated. Viton-A was readily dissolved by carbon dioxide with acetone cosolvent. This key finding may form the basis for an environmentally friendly process for the recycling of pyrotechnic and other energetic materials.

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RECOVERY OF PYROTECHNIC INGREDIENTS USING SUPERCRITICAL FLUIDS

SBIR Phase I Final Report
for the period May 16, 1996 to December 31, 1997

Contract No. N00164-96-C-0049

Prepared by

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January 21, 1998

IDENTIFICATION AND SIGNIFICANCE OF PHASE I WORK

Summary

The Phase I program studied the recovery of constituents from a Magnesium-Teflon-Viton (MTV) pyrotechnic material. In particular, we investigated the use of near critical liquid and supercritical carbon dioxide with acetone cosolvent to dissolve the Viton-A binder component. We found Viton-A to be readily dissolved by carbon dioxide with acetone cosolvent. This key finding may form the basis for an environmentally friendly process for the recycling of pyrotechnic and other energetic materials.

Background

The Navy has numerous pyrotechnic munitions that require demilitarization. Many of these contain valuable resources that could be used in commercial applications, for example metals (e.g. magnesium, aluminum), metallic salts of copper, strontium, and barium, oxidizer (e.g. sodium nitrate, potassium perchlorate), binders such as Viton, and dyes. The Navy is seeking technology that can recover the valuable ingredients from pyrotechnic flares and smoke munitions in an environmentally acceptable manner. The present study is relevant to this goal, and is applicable to materials from existing decommissioned stockpiles, as well as to the formulation of new propellant, explosive, and pyrotechnic (PEP) materials designed to minimize adverse environmental life-cycle effects. In particular, we have investigated the application of near critical and supercritical carbon dioxide to the removal of binder from a Magnesium-Teflon-Viton (MTV) pyrotechnic material.

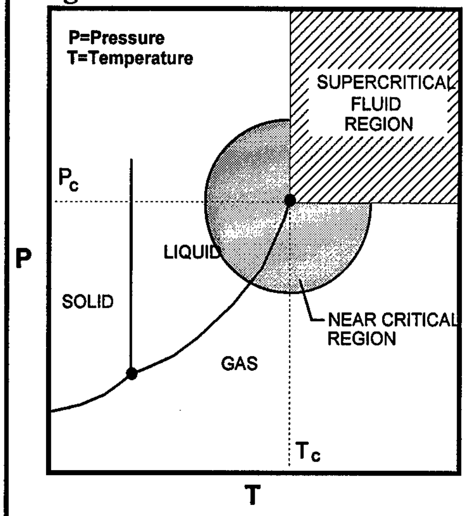
Supercritical Fluids

Over the past decade, environmentally friendly solvents known as supercritical fluids have been increasingly investigated and employed as a substitute for conventional organic solvents. As such fluids may not be a familiar concept, a brief characterization is given below.

Referring to the pressure-temperature diagram in Figure 1, a pure compound enters its supercritical fluid region at conditions that equal or exceed both its critical temperature and critical pressure. These critical parameters are intrinsic thermodynamic properties of all sufficiently stable pure component compounds. Carbon dioxide, for example, becomes supercritical at conditions that equal or exceed its critical temperature of 31.1°C and its critical pressure of 73.8 bar (1,055 psig). In the supercritical or near-critical fluid region, normally gaseous substances, such as carbon dioxide, become dense phase fluids that can exhibit greatly enhanced solvating power as compared to the gaseous state. For example, at a pressure of 208 bar (3,000 psig) and a temperature of 40°C, carbon dioxide has a density of about 0.8 g/cc and has been compared to organic solvents such as toluene, acetone or hexane (Rindfleisch, 1996).

A near-critical or supercritical fluid can display a wide spectrum of solvation power because its density is strongly dependent on both temperature and pressure. Temperature changes of tens of degrees Celsius or pressure changes by tens of atmospheres can change solubility by an order of magnitude or more. This unique feature facilitates solute recovery, the "fine-tuning" of solvation power and the fractionation of mixed solutes. The selectivity of nonpolar near-critical or supercritical fluid solvents can be further enhanced by the use of small concentrations of polar entrainers or cosolvents such as ethanol, methanol, or acetone. Near-critical or supercritical fluid solvents with/without cosolvents are hereinafter jointly referred to as critical fluids.

Figure 1: Supercritical Fluid Diagram



In addition to its unique solubilization characteristics, a critical fluid possesses other physicochemical properties that add to its attractiveness as a solvent. A critical fluid solvent can exhibit a liquid-like density and, at the same time, gas-like properties of viscosity and diffusivity. The latter increases mass transfer rates, significantly reducing processing times. Additionally, the ultra-low surface tension of a critical fluid allows facile penetration into microporous materials, increasing extraction efficiency and overall yields. Critical fluid technology is well established in other industries such as the decaffeination of coffee and extraction of hops.

The readily adjusted solubility of compounds in critical fluids is the basis of a number of precipitation processes that have appeared in the literature. The technique of varying solubility to cause precipitation is limited, however, by the fact that the compound of interest must have significant solubility in the supercritical fluid for at least some temperature and pressure conditions. Many materials of interest, including many PEPs, are too polar to dissolve to any extent in supercritical fluids and hence do not fulfill this criterion. It is this limitation that has led to the development of the gas antisolvent (GAS) technique, which name refers to the fact that compressed gases (or liquefied or supercritical gases) are used as antisolvents. In this method, a compressed fluid is added to a conventional organic liquid solvent containing the solute to be crystallized. If compressed gas is used as the antisolvent, its dissolution into the solvent is typically accompanied by a reduction in density and change in polarity of the solvent mixture, and consequently, a reduction of the liquid's solvation power relative to a particular substance. As a result, the mixture becomes supersaturated, which causes crystals to form. If a supercritical fluid or liquefied gas is used as the antisolvent, however, the mixture density may actually be greater than that of the neat solvent. In this case, precipitation is presumably caused primarily by the polarity change of the mixture. In the GAS crystallization process, it is essential that solids have low solubility in the selected compressed fluid.

The GAS process was developed by Krukonis and coworkers (Gallagher, et al., 1989, 1991a, 1991b, 1992) in the earliest work applying critical fluids to PEPs. In these studies, supercritical CO_2 antisolvent was used to precipitate void-free crystals of various size ranges. Void-free crystals are desirable for optimum munition and propellant performance, but are very difficult to produce by conventional means. The systems studied included cyclotrimethylenetrinitramine (RDX) dissolved in either cyclohexanone or acetone, RDX and cyclotetramethylenetetranitramine (HMX) mixtures dissolved in γ-butyrolactone or dimethylsulfoxide (DMSO), and nitroguanidine (NQ) dissolved in pyrrolidone or N,N-dimethyl formamide. In all cases it was found possible to generate void-free particles of the desired shape and size, the latter being anywhere from < 5 µm to 200 µm. Furthermore, substantial separation of HMX from RDX in the mixed solutions was found to be possible.

Watkins and Krukonis (1991) evaluated the fractionation and extraction of hydroxy-terminated polybutadiene (HTPB) and of glycidyl azide polymers (GAP) using near critical and supercritical fluids as direct solvents. Such a fractionation could be useful in obtaining binder with a narrow molecular weight distribution, improving the consistency of propellant characteristics. The solvents tested included propane, CO_2, and Freon 22. For HTPB, propane could give fractionation across the entire molecular weight spectrum, while for GAP Freon 22 could give fractionation across the entire molecular weight spectrum. For both polymers, CO_2 could only dissolve the lower molecular weight fractions.

The most extensive effort on the use of supercritical fluids with PEPs has been the application of supercritical water oxidation (SCWO) for compound destruction. Over the past 5 years, General Atomics has been involved with a pilot-scale SCWO program involving the destruction of solid rocket motors for the U.S. Air Force (Downey, 1995). In a separate program, Sandia National Laboratory has been working with the U.S. Army in applying SCWO to the destruction of smoke-forming materials, dyes, and pyrotechnics (Rice, et al., 1994). SCWO is of secondary interest to the present program as it would reduce the pyrotechnic constituents to basic forms with very low value. Even in the absence of oxygen, magnesium will react with high temperature water to give magnesium oxide and hydrogen gas.

Magnesium-Teflon-Viton (MTV) Pyrotechnic

It was determined through discussions with the Navy that the focus of the present investigation would be on MTV, a Class 1.3 explosive that burns at very high temperature. It is used as infrared decoy flares and for ignition of solid propellant rocket motors. The composition of MTV is shown in Table 1.

Table 1. Composition of MTV from MIL-I-82736A(OS)

Ingredient	Applicable Document	Min. wt%	Max. wt%
Mg powder, Type II, Granulation 16	MIL-M-382	52.5	54.5
Plastic Molding Material (PTFE)	D 1457-83 Type IV	29.5	32.0
Copolymer, Vinylidene Difluoride and Hexafluoropropylene	WS 7682	15.0	16.5

The copolymer shown in Table 1 refers to Viton-A (made by DuPont Dow) or in some cases an equivalent polymer known as Fluorel (made by Dyneon, a joint enterprise of 3M and Hoechst). Both Viton-A and Fluorel are random copolymers of vinylidene difluoride and hexafluoropropylene, with 78 mol% of the former and 22 mol% of the latter. The copolymer may contain small amounts of polymerization catalysts, coagulants, antioxidants, or curing terminal groups, but must be >99.5% soluble in acetone (WS 7682, 1968). The conventional process for manufacture of MTV, known as "shock-gel", involves dissolving Viton-A in acetone then adding magnesium and Teflon powders to make a paste-like slurry (Renner, et al., 1995). The paste is then mixed with hexane, which serves as an antisolvent, causing precipitation of the Viton-A onto the magnesium and Teflon particles to bind them. After decantation of the hexane-acetone supernatant, the precipitate is further washed with hexane to remove residual acetone. The precipitate is then dried to yield a free-flowing MTV "crumb". The next manufacturing step is extrusion in round or cruciform strands of 0.090-0.098" diameter. The extrusion takes place at about 121°C, and 400 bar (5800 psig) and 830 bar (12,000 psig) for rounds and cruciforms, respectively. Finally, the strands are cut to a length of 0.150-0.228".

For MTV pellets to be accepted for use by the military, the MTV crumb from which they were formed must be analyzed for copolymer content. This is done by allowing approximately 1 gram of MTV crumb to soak in 100 ml of acetone for at least 16 hours at room temperature, and determining the weight loss. As is evident from this procedure the binder in MTV crumb is readily soluble in acetone; however, the same may not be true of the extruded material (Renner, et al., 1995). The heat or pressure from the extrusion may cause cross-linking (vulcanization) of the Viton-A. Wall (1972) reports that magnesium oxide is a cocatalyst for the cross-linking process, so the magnesium in the MTV formulation may also play a role in causing insolubility.

An alternative method for the manufacture of MTV has recently been suggested by Farncomb and Nauflett (1996a). In this method, designated "super-shock", the hexane antisolvent of the conventional process is replaced with supercritical CO_2. In this manner, mixed organic solvents are avoided and recovery of pure acetone and CO_2 for reuse is greatly simplified. While the conventional shock-gel process produces about 10 lbs of hazardous waste for every lb of MTV product, the super-shock process produces only one tenth this amount (Farncomb and Nauflett, 1996b). Disposal of the mixed organic solvent from the shock-gel process costs $600 per 55 gallon drum. Farncomb and Nauflett (1996a) demonstrated that off-spec MTV crumb could be reprocessed using the super-shock technique to manufacture high-quality MTV.

The earliest study on recovery of materials from extruded MTV appears to have been initiated by Battelle in the 1970's and subsequently carried on by Tracor (Johnson, 1997). This process utilized a mixed solvent comprised of 65% butyl acetate, 10% amyl acetate and 25% methylene chloride. Contacting flare materials with this solvent and vigorous agitation for a period of several hours extracted about 90% of the copolymer binder. The use of mixed, chlorinated solvent, however, is not attractive in environmental terms.

Fluoropolymer Solubility in Critical Fluids

Recently, McHugh and coworkers at Johns Hopkins have investigated the solubility of various fluoropolymers, including Viton-A and Fluorel, in neat supercritical carbon dioxide and in supercritical carbon dioxide with acetone cosolvent. DiNoia, et al. (1996) found that Viton-A was insoluble in CO_2 at temperatures up to 284°C and pressures up to 2200 bar. As Viton-A can potentially be contaminated with a barium sulfate residue from manufacture, it was pretreated by washing with hydrochloric acid and water, or by dissolving in acetone and filtering. Neither of these procedures was successful in yielding miscibility of CO_2 and Viton-A. Furthermore, while the Viton-A could be completely dissolved in pure acetone at room temperature (proportions not given), it could not be dissolved in supercritical CO_2 containing 24.9 wt% acetone cosolvent (presumably at a Viton-A concentration of about 5 wt%).

Surprisingly, much different behavior was found for the supposedly equivalent material, Fluorel. Fluorel exhibited single-phase behavior with CO_2 at conditions as mild as 75°C and 700 bar. With the addition of 27 wt% acetone as a cosolvent, Fluorel exhibited 4 wt% solubility at conditions as mild as 21°C and 47 bar. The reason for this unexpected difference from Viton-A is unknown, but DeNoia, et al. (op. cit.) suggest the possibility of different functional end groups on the polymer chains or the presence of other additives. Another explanation may be the type of Viton-A or Fluorel used. There are over 10 types of Viton-A supplied by DuPont Dow, which vary in the amounts of accelerator, curative, and "process aid" used in the formulation (DuPont Dow, 1996). Likewise, Fluorel is a family of products with many variations (Dyneon, 1997).

A limitation of the results of McHugh and coworkers may be in the narrow composition range employed to determine solubility. Their see-through apparatus was typically charged with about 5 wt% propellant and 95 wt% solvent. The apparatus was then magnetically stirred, and the transition point from cloudy to clear used to indicate the transition from a two-phase mixture to a single phase. With this procedure, materials soluble at less than 5 wt% would be classified as insoluble.

In view of the prior published work described above, it was clear that the binary extraction system of CO_2-acetone would be a primary candidate. Use of a binary solvent system complicates the phase behavior in that one must now be concerned with a critical line, in this case connecting the critical points of the two pure components, rather than just the critical point of a single compound. The two fluids are in general not completely miscible under all pressure/temperature/composition conditions, and unexpected solubility behavior may be encountered if a phase boundary is inadvertently crossed. Fortunately, the phase behavior of the CO_2-acetone system in the region of interest has been determined by Page and coworkers (1993). This allowed the experiments to be carried out under known single-phase conditions. Figure 2 illustrates the phase behavior for the CO_2-acetone system.

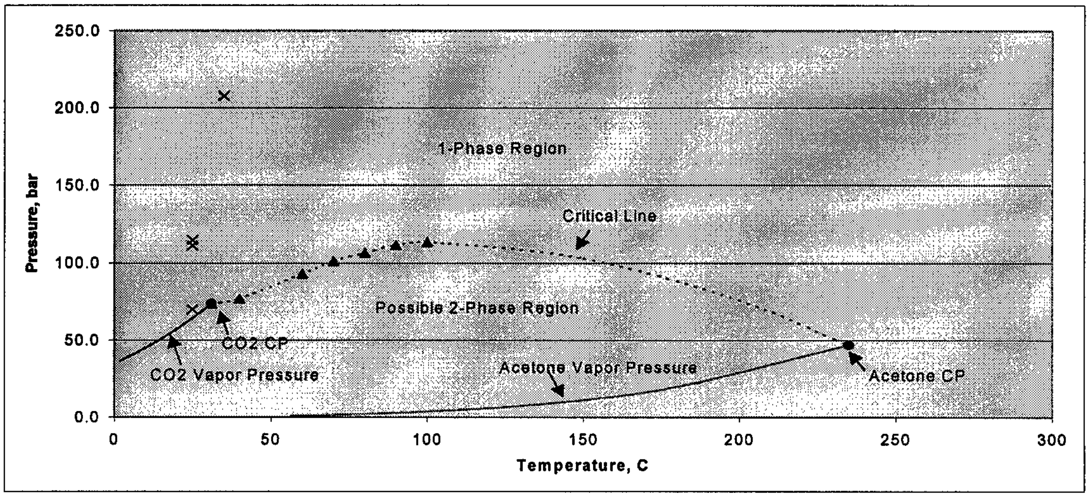


Figure 2. CO2-acetone system phase behavior.

In Figure 2, critical line data derived from Page, et al. (op. cit.) is indicated by triangles. The dotted line indicates an approximate course of the CO_2-acetone critical line. The two-phase region for this simple system is found at pressure and temperature coordinates within the bounds of the two vapor pressure curves and the critical line. Experimental conditions for the current tests (see below) are indicated by an x, and are seen to be outside of the two-phase region.

Experimental

Materials

Preliminary tests were carried out with Viton O-rings of unknown specification. The carbon dioxide used was technical grade obtained from Associated Gas Products (Everett, MA) with a purity of 99%. Acetone and other solvents were Baker analytical grade. Prior to working with MTV, a Class 1.3 explosive, handling and storage procedures were documented and reviewed by Mr. Dick Lowell of the Defense Logistics Agency (Pease Air National Guard Base, NH). The MTV crumb utilized was obtained from the Naval Surface Warfare Center (NSWC) at Crane, IN. The batch was manufactured specifically for this program according to conventional procedures using an igniter formulation. A shipment of 25 g was received from NSWC Crane in a protective pipe casing. At Aphios, the material was stored in a grounded ammunition magazine, supplied courtesy of Loral Hycor, Woburn, MA.

Apparatus and Procedures

The Phase I investigation included two sets of experiments, the preliminary static (no flow) extraction tests, and the dynamic (flow-through) extraction tests. Some of the static tests were carried out at ambient pressure in glass beakers. Other static tests utilized near critical liquids or supercritical fluids, and were carried out in an apparatus similar to that shown in Figure 3.

Prior to the start of testing, the system was pressure tested at 550 bar (8000 psig). For a static high pressure extraction test the substrate, usually a Viton O-ring, and a cosolvent if used, were first placed in the 0.5 ml extraction vessel (ID = 0.635 cm) within an Isco (Lincoln, NE) SFX 2-10 Extractor. Critical fluid from a high-pressure syringe pump fitted with a cooling jacket was then used to bring the system to the desired pressure. The extractor temperature was achieved by heaters integral to the SFX 2-10 Extractor. After the desired soak time, the system was depressurized. The O-ring was retrieved and allowed to outgas at ambient conditions. The O-ring was then weighed and visually inspected to determine if any dissolution had occurred.

Dynamic extraction runs used the system shown in Figure 3. To start a dynamic extraction run, about 0.25 g of MTV crumb was first loaded into the extraction chamber. The system was then pressurized with carbon dioxide from the critical fluid syringe pump, in conjunction with a Tescom back pressure regulator. After coming to temperature, CO_2 and acetone flows were commenced at the desired ratio. The mixed solvent passed through the extraction chamber, depressurized as it passed through the back pressure regulator, and acetone and solute were deposited within a collection vessel.

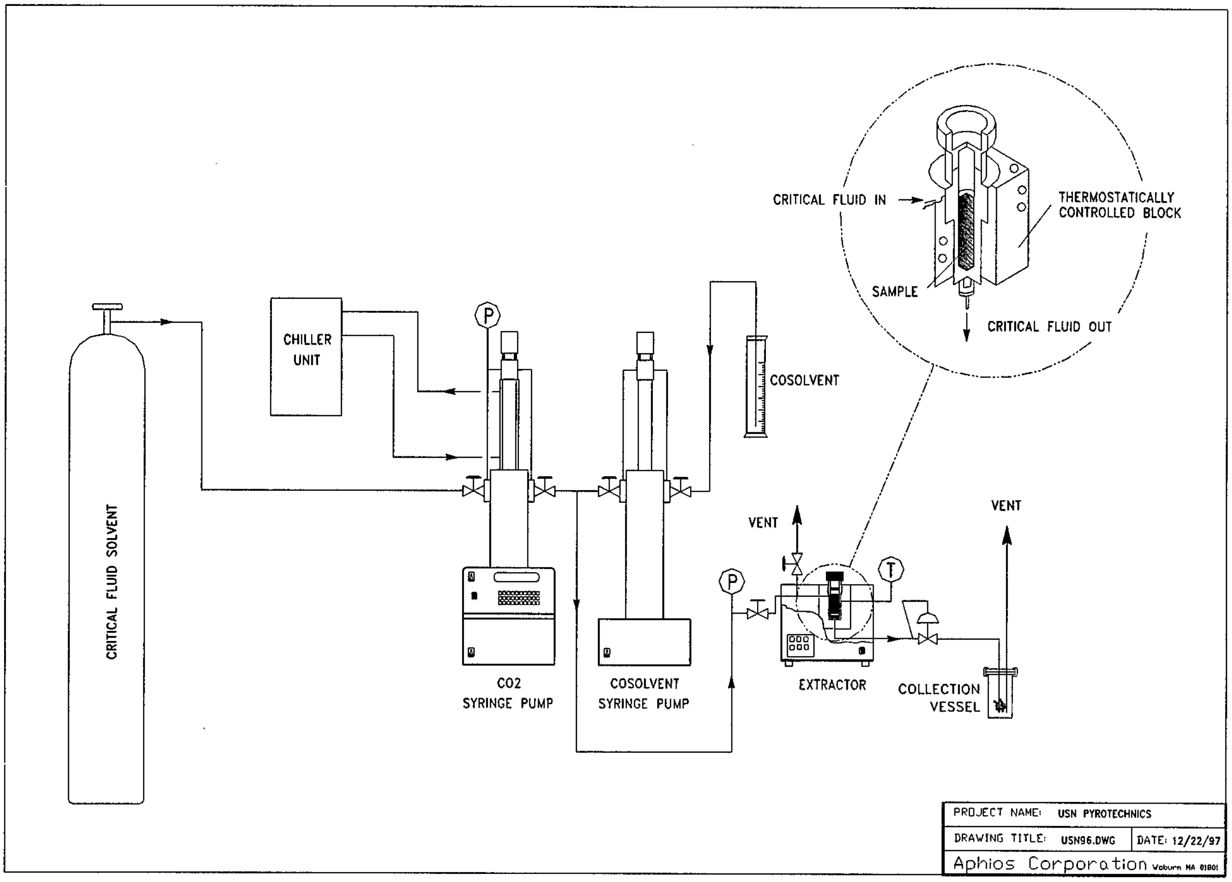


Figure 3. Critical fluid extraction apparatus.

With the exception of the glass collection vessel, system wetted parts were comprised entirely of 316 stainless steel or Teflon.

Subsequent to a dynamic run, MTV residue was collected from the extraction chamber and weighed. Percentage weight loss was determined to assess the degree of binder extraction. Magnesium and Teflon are not significantly soluble in the solvents used for these tests.

Results and Discussion

Receipt of MTV material was delayed for some months in order for the shipping protocols from the Navy to be approved. In order to make progress in the meantime, a set of preliminary static extraction experiments was undertaken using generic Viton O-rings. The results of these tests are shown in Table 2. A wide variety of solvents was tested, including near critical and supercritical CO_2, CO_2 with acetone cosolvent, near critical and supercritical Freon 22 ($CHClF_2$), the Tracor solvent described earlier, and other solvents which the literature suggested were incompatible with Viton. While swelling was noted in many cases, even by as much as a factor of 2, the only apparent lasting effect was some blistering or splitting of the O-ring. After solvent evaporation or outgassing, no weight loss was observed in any O-ring test.

In an effort to encourage solvation, an O-ring was frozen in liquid nitrogen and shattered with a hammer. The resulting increase in surface area did not, however, result in any increased solubilization. The lack of solubilization may indicate that the O-ring was of a crosslinked type of Viton-A, or of a type of Viton other than Viton-A. Viton-B and Viton-F are terpolymers that contain not only vinylidene difluoride and hexafluoropropylene, but also tetrafluoroethylene. These Viton types have increased solvent resistance (DuPont Dow, 1996).

The final entry of Table 2 is the one static experiment carried out with MTV crumb. This test verified the effectiveness of the Tracor solvent in extracting essentially all of the Viton-A binder. The loss of more than the expected 16 wt% binder content is attributed to losses during handling of the MTV.

Table 2. Summary of Static Experiments

Run No.	Substrate	Temp. °C	Pressure bar (psig)	Solvent	Extraction time	% Wt Loss
3a	Viton O-ring	25	84 (1200)	CO_2	10 min	0
3b	Viton O-ring	51	249 (3600)	CO_2	10 min	0
3c	Viton O-ring	51	235 (3400)	CO_2	10 min	0
3d	Viton O-ring	100	518 (7500)	CO_2	10 min	0
3e	Viton O-ring	26	84 (1200)	CO_2	30 min	0
5a	Viton O-ring	25	91 (1300)	$CHClF_2$	10 min	0
5b	Viton O-ring	51	242 (3500)	$CHClF_2$	10 min	0
5c	Viton O-ring	99	504 (7300)	$CHClF_2$	10 min	0
5d	Viton O-ring	25	Ambient	Acetone	12 hrs	0
5e	Viton O-ring	25	Ambient	CH_2Cl_2	12 hrs	0
6a	Viton O-ring	26	84 (1200)	50/50 v/v CO_2 /Acetone	60 min	0
6b	Viton O-ring	51	249 (3600)	50/50 v/v CO_2 /Acetone	60 min	0
7a	Viton O-ring	25	Ambient	Acetone	21.5 hrs	0
7b	Viton O-ring	25	Ambient	n-Butyl acetate	21.5 hrs	0
7c	Viton O-ring	25	Ambient	Ethyl acetate	21.5 hrs	0
7d	Viton O-ring	25	Ambient	Toluene	21.5 hrs	0
8	Viton O-ring	25	Ambient	65% BuAc/ 10% Amyl acetate/ 25% CH_2Cl_2	17.5 hrs	0
9	Viton O-ring	25	Ambient	Tetrahydrofuran	21 hrs	0
10	Ground Viton O-ring	25	Ambient	65% BuAc/ 10% Amyl acetate/ 25% CH_2Cl_2	23.5 hrs	0
11	0.5 g MTV crumb	25	Ambient	65% BuAc/ 10% Amyl acetate/ 25% CH_2Cl_2	24 hrs	21

Results from the dynamic extraction tests are given in Table 3. All of these tests utilized 0.25 g of MTV crumb. The first two experiments listed are controls with pure CO_2 and pure acetone.

As expected, the CO_2 extracted essentially no binder (the 1% weight change is probably due to transfer losses) while the acetone gave essentially complete extraction. The remainder of the table shows the carbon dioxide-acetone cosolvent tests, all of which used 20 vol% acetone. (At the pressure and temperature conditions used, volume percent and weight percent are essentially equivalent.) Lower pressure and temperature conditions were emphasized with an eye toward minimizing the cost of an eventual commercial process. As shown in Table 3, duplicate experiments were run at two conditions. Runs 26 and 30 were both conducted at 1.0 ml/min for 120 minutes and gave weight losses of 11%. Runs 27 and 33 were both conducted at 2.0 ml/min for 60 minutes and gave weight losses of 17% and 18%, respectively. Both duplicate sets used a pressure of 70 bar (1,000 psig) and a temperature of 25°C. Thus, reproducibility appears to be excellent.

The sixth and seventh columns in Table 3 give the amount of solvent and cosolvent used for each experiment. While minimization of solvent usage was not rigorously evaluated in these tests, it should be noted that Run 32 utilized the lowest amount, a total of 15 g. Given that 0.25 g of MTV crumb was used, the weight ratio of solvent + cosolvent to crumb was about 60. Assuming a Viton-A content of about 15 wt%, the weight ratio of solvent + cosolvent to Viton-A was about 400. In view of this high solvent ratio, the results of Table 3 are not necessarily inconsistent with the previously mentioned results of DiNoia, et al. (1996), who reported that Viton-A, presumably at a level of about 5 wt%, could not be dissolved in supercritical CO_2 with 24.9 wt% acetone cosolvent.

Table 3. Summary of Extraction Experiments in Flow Apparatus

All tests utilized 0.25 g MTV crumb. All cosolvent tests used 20 vol% acetone.

Run No.	Temp °C	Pressure bar (psig)	Total flow ml/min	Extraction time minutes	CO_2 g	Acetone g	% Wt Loss
13	25	70 (1000)	0.5	30	12	0	1
18	25	Ambient	0.5	120	0	47	17
25	25	70 (1000)	1.0	30	19	5	6
26	25	70 (1000)	1.0	120	77	19	11
27	25	70 (1000)	2.0	60	77	19	17
28	25	70 (1000)	2.0	30	39	9	7
29	25	70 (1000)	1.0	60	39	9	10
30	25	70 (1000)	1.0	120	77	19	11
31	35	208 (3000)	1.0	60	39	9	24
32	35	208 (3000)	1.0	18	12	3	16
33	25	70 (1000)	2.0	60	77	19	18
34	25	111 (1600)	2.0	30	39	9	18
35	25	115 (1650)	1.0	60	39	9	17

The effect of extraction time on amount extracted is shown for two different flow rates in Figure 4. At 2 ml/min, binder appears to be linearly extracted up to the point of complete extraction. This seems reasonable because the Viton should be on the surface of the particles, and subject to minimal diffusion limitations. At 1 ml/min, on the other hand, extraction starts off in a linear fashion but then tails off well before achieving full extraction. A possible explanation for this behavior is consistent fluid bypassing within the extraction chamber, i.e., the binder in the active flow path is depleted within about 60 minutes while the binder in stagnant areas is leached only slowly. The result at 120 minutes was consistent in duplicate runs, and thus appears not to be an anomaly. If the interpretation given here is correct, it suggests that intimate contact of the MTV substrate and the extracting solvent is very important.

A second point of interest in Figure 4 is apparent from comparing the two data points at 30 minutes. At the higher flow rate, twice as much solvent has passed through the sample as compared to the lower flow rate, yet the amount of material solubilized is about the same. Thus, the fluid at the higher flow rate must be far from the Viton-A solubility limit, and is not being used in the most efficient manner. This same conclusion is reached by comparing Run 32 of Table 3 with other runs that gave 16 wt% or higher extraction. While all of these runs extracted essentially all of the Viton-A, Run 32 used considerably less solvent to do so. Efficient solvent usage will become important in scaled-up designs for this extraction process, and will be one of the issues addressed during a Phase II program.

Most importantly, the results of Table 3 and Figure 4 indicate the feasibility of complete binder extraction using the CO_2-acetone solvent system.

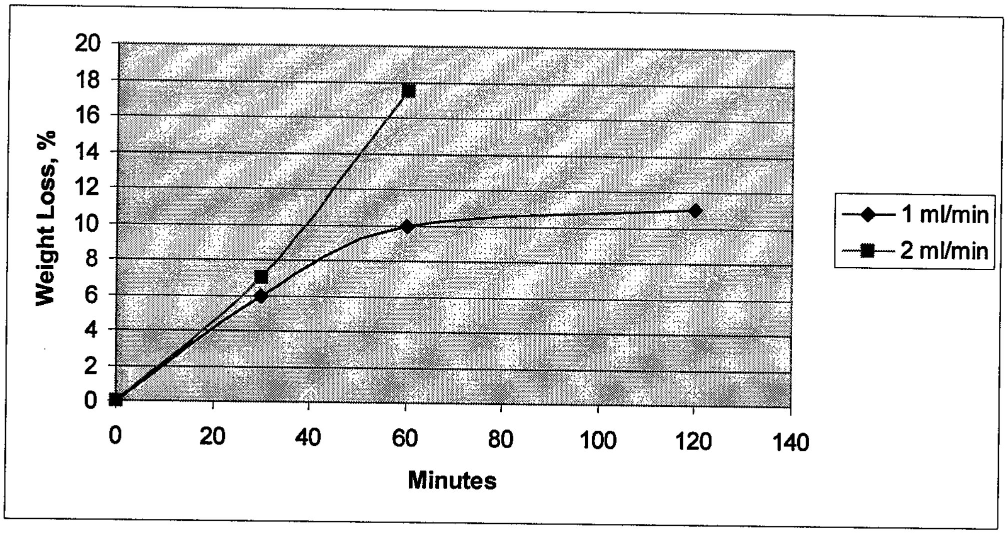


Figure 4. MTV weight loss vs. time at two different flow rates. Solvent is 20% acetone in CO_2, temperature = 25°C, pressure = 1,000 psig. Each data point represents a separate experiment.

Commercial Contacts

Over the course of the Phase I program, a number of contacts were made with potential commercial clients or partners. The companies contacted are summarized in Table 4. Further comments on these contacts follow.

Table 4. Contacts with Potential Commercial Clients/Partners

Company	Contact	Phone
Alliant Tech	Al Dane	(901)658-5231
Eagle-Picher	Dolph Hubbard	(417)623-3660
Ensign-Bickford	Joe Susco	(203)843-2864
Hart Metals	Larry Bender	(717)668-0001
Loral Hycor	Danny Sullivan	(781)935-5950
Martin Electronics	Jim Hamilton	(904)584-2634
Reade Manufacturing	Mitchell Markovitch	(908)657-6451
TPL	Franklin Kroh	(505)344-4444
Tracor	Alvin Carter	(501)574-1712

Alliant Tech, Kilgore, TN manufactures MTV and other magnesium-teflon products. They mentioned that premium specification magnesium powder is worth $50-$70 per pound and stated that magnesium is by far the most valuable constituent of the pyrotechnic mix.

A contact with Ensign-Bickford, Simsbury, CT, was made at the suggestion of Mr. Bob Farncomb of the Naval Surface Warfare Center at Indian Head, MD. However, Ensign-Bickford does not use MTV material.

Hart Metals, Pittsburgh, PA, is a magnesium processor that buys their magnesium from Alcoa in the form of ingots. They grind and atomize the magnesium, which they then sell to governments around the world. They evaluated a sample of MTV crumb from which we had extracted the Viton, leaving a residual composition of about 37 wt% Teflon and 63 wt% magnesium. For reclaimed magnesium to be of interest to them, it would have to have a purity of at least 82-85%. Due to space limitations at their existing facilities, they are not interested in installing additional magnesium processing equipment that would allow them to accept lower purity material. Hart expects that any magnesium we produce from our process will be of relatively low grade, commanding a price of only about $1.00/lb. The best we could hope for is probably about $3.00/lb. Hart Metals is interested in our activities as a potential client or collaborator. A letter of interest from Hart is provided as attachment A.

Loral Hycor, Woburn, MA does not use MTV material. They referred us to Eagle-Picher, which manufactures magnesium-Teflon formulations but not MTV. Eagle-Picher purchases about 50 lbs of magnesium-Teflon per year from Tracor.

Martin Electronics, Perry, FL, is one of the three current commercial manufacturers of MTV material. They manufacture IR decoy flares for the Navy, and buy magnesium that conforms to strict military standards. A different grade of material could not be used without Navy approval, undoubtedly a long and complicated undertaking. They do not know of any commercial uses for MTV.

Reade Manufacturing, Lakehurst, NJ, is a magnesium processor. They evaluated a sample of MTV crumb from which we had extracted the Viton. As was stated by Hart Metals, the Teflon must be removed in order to generate a useful magnesium product.

Tracor manufactures MTV at Camden, AR. A Dr. Evans of Tracor carried out the organic solvent extraction study mentioned above circa 1980. He retired shortly thereafter. Tracor knows of no civilian uses for MTV.

TPL, Albuquerque, NM, has recently completed a Phase I SBIR on the Reclamation and Reuse of Pyrotechnic Ingredients. Through its U.S. Army Pyrotechnic Munitions Demilitarization program, TPL has experience in disassembly, reclamation and reprocessing procedures for many munitions of interest to the U.S. Navy. According to Hart Metals, TPL has produced magnesium of suitable quality at a small scale, but the product of the scaled-up process was unsatisfactory. The MTV which TPL has been focussing on derives from a composition containing 60-70% Mg, 5-7% Viton, and the balance Teflon. The material is contained in flares holding about 4-6 lbs of magnesium each.

One question of interest to any commercial entity is the amount of recovered product that would be available. The known stockpile of the type of MTV we investigated is about 15 tons (Johnson, 1997). To an MTV manufacturer or magnesium processor, this represents a relatively small quantity of material and is not a great financial incentive. As previously mentioned, however, the process should be applicable to many other PEP materials.

Conclusions

The key finding of the present study is the ready dissolution of Viton-A binder from MTV crumb. This result may serve as the basis for an environmentally friendly process for the recycling of pyrotechnic materials, one that eliminates the use of chlorinated solvents and minimizes the use of other organic solvents. Viton and other fluoropolymers are used as binders in a number of propellant, explosive, and pyrotechnic materials, so that the results presented here are of interest to a fairly wide variety of materials.

The commercial market for the products that may result from a mature version of the present process is unclear at this point. It seems likely that a route to recycle the magnesium would be available, although its value may be relatively low. Aftermarkets for Teflon have not yet been investigated. The armed forces may be able to use reclaimed materials such as magnesium in training rounds, for which requirements are less stringent. The most important economic driver for the process may in fact be the avoided cost, i.e., eliminating perpetual storage of hazardous stockpiles and their potential liabilities.

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