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**EVALUATION OF POLYSTYRENE HOLLOW PLASTIC SPHERES
TO ENHANCE HYDRAULIC FLUID COMPRESSIBILITY**

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U.S. ARMY ARMAMENT RESEARCH AND DEVELOPMENT CENTER

LARGE CALIBER WEAPON SYSTEMS LABORATORY

DOVER, NEW JERSEY

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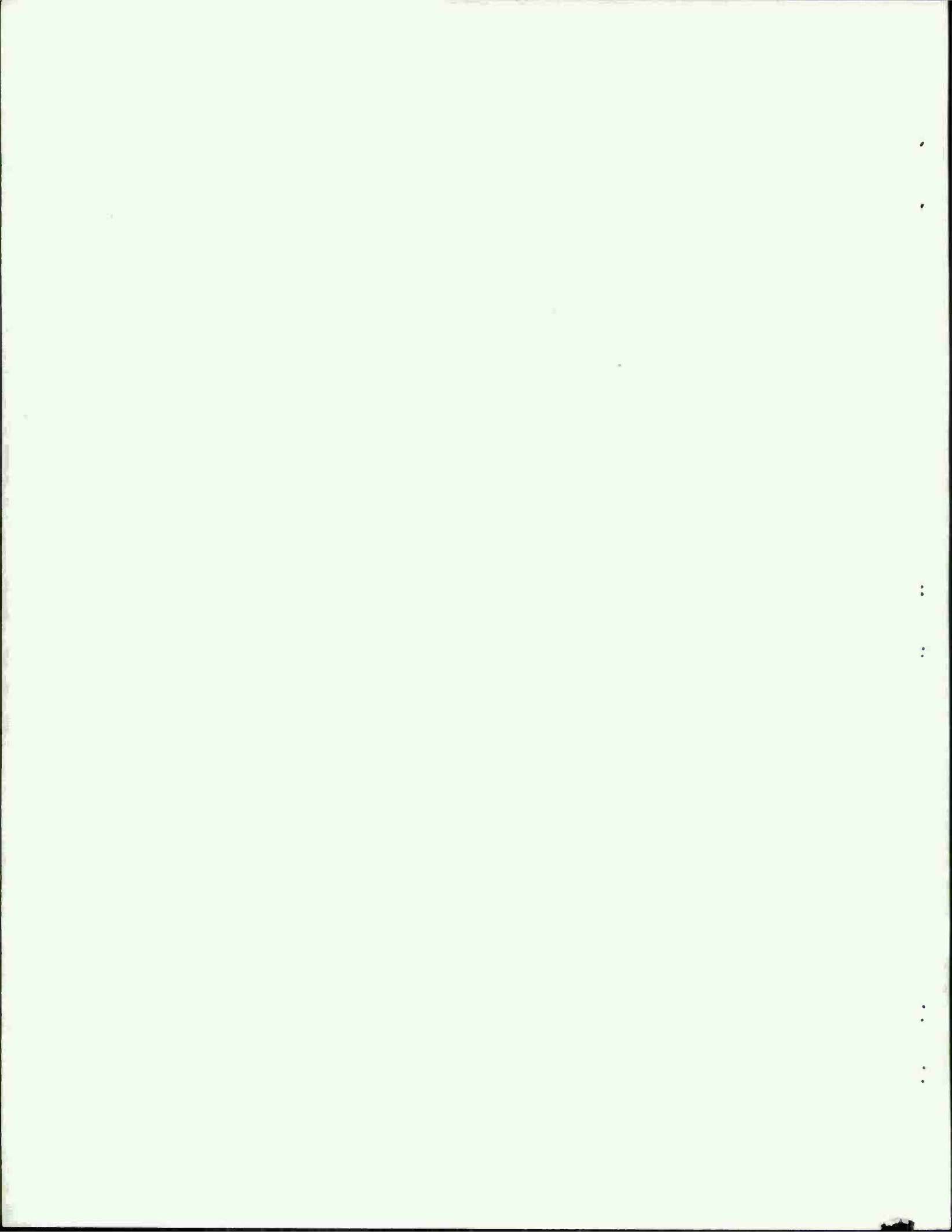
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FOREWORD

The Enhanced Compressible Fluid Technology Program is being conducted under 6.1 research funding by the Weapons Division of the Large Caliber Weapon Systems Laboratory (LCWSL), U.S. Army Armament Research and Development Center (ARDC), Picatinny Arsenal, Dover, NJ.

The goal of this program is to determine an optimum fluid for use in a compressible fluid recoil mechanism (CFRM). This mechanism, designed by the LCWSL, was live-fired at ARDC and met or surpassed all operating requirements when used with silicon oil (Dow Corning silicone 200).

One of the options pursued under the program was the suspension of balloon-like plastic spheres in the recoil oil to increase its compressibility. As the result of a feasibility study conducted by ARDC, such a fluid was formulated and manufactured by Rohm and Hass Company under contract to National Space Technology Laboratory. Laboratory tests were performed by Rohm and Haas and a supply of this fluid, suitable for dynamic testing in the Compressible Fluid Test Fixture (CFTF), was furnished to ARDC. Laboratory test results, as well as design and production information, are included in this report.



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INTRODUCTION

The US Army Armament, Munitions, and Chemical Command (AMCCOM) Large Caliber Weapons Systems Laboratory (LCWSL) at Picatinny, New Jersey, is evaluating techniques for improving the compressibility of the fluids used in the recoil chambers of large caliber weapons. A new concept utilizing a radically different recoil system proposes to utilize the fluid as a means of dissipating energy. A possible improvement to energy dissipation by these fluids is to use polymers in the form of small hollow plastic spheres (HPS) dispersed in the hydraulic fluids of recoil mechanisms. The resulting compressible sphere-hydraulic fluid mixture may improve the performance of the recoil process while decreasing the total amount (volume) of fluid required in the compressible fluid recoil mechanism and concurrently enhancing the compressibility characteristics of the fluid.

The feasibility of using polymeric materials for candidate HPS was evaluated in two recent reports.^{1,2} Of the twelve polymers investigated, the physical and chemical properties of fluorinated ethylene propylene (FEP, a Teflon) and polyvinylidene fluoride (PVDF) were shown to possess the best characteristics for compressibility. However, these two polymers are considered to be two of the most difficult materials lending themselves to micron-size HPS construction. Results of industrial survey indicate that current technology is unable to produce hollow plastic spheres of these materials.

Although the highly crystalline nature of polystyrene (PS) limits the compressibility of the polymer,^{1,2} it was recommended as being the easiest and most feasible HPS to produce. The mechanical properties of polystyrene indicate that an acceptable volumetric compressibility can also be attained with this polymer. In addition, polystyrene HPS have been produced as a 20% by weight (W/W) dispersion in DC-200 (1Q), a Dow Corning silicone fluid with a viscosity of 10 cs at room temperature.³ This silicone fluid has been found to exhibit a compressibility of 2.6% at 5000 psig and -46°C.⁴

A sphere size for designing HPS for optimum compressibility was also recommended.^{1,2} The two parameters having the greatest influence on sphere compressibility were determined to be (1) sphere radius and (2) wall thickness. A sphere of approximately 0.4 micron diameter and a wall thickness of approximately 0.08 microns was selected as the best radius for forming a stable suspension of HPS in silicone fluid and the most feasible wall thickness at that radius for producing compressible PSHPs.

The USAAMCCOM tasked the Engineering Laboratory of Computer Sciences Corporation (CSC-EL) at the National Space Technology Laboratories, NSTL, MS, to support the LCWL in evaluating the effectiveness of PSHPs for enhancing the

compressibility of recoil fluids. AMCCOM requested that CSC-EL produce 20 pounds of 45-50 weight percent of 0.4 micron PSHPs in DC-200 (10) silicone fluid or, the maximum amount of PSHPs the silicone fluid can accommodate. The tasking specified that the spheres of this dispersion were to be silanized (silicon-coated) for increased compatibility with the silicone fluid and a stable dispersion produced. Additionally, AMCCOM requested that the spheres be instrumentally analyzed, and the dispersion undergo viscosity and high temperature/high pressure compressibility testing. The instrumental analyses confirmed the consistency and continuity of the spheres and their surface characteristics. The compressibility tests evaluated the ability of the spheres to remain structurally and chemically intact under the extreme environmental conditions. The viscosity tests were required to determine the behavior and stability of the solution with its high-solids (sphere) content.

APPROACH

The CSC-EL subcontracted Rohm and Hass Company, Spring House, PA, to prepare 24 pounds of 40% (W/W) dispersion of silanized, 0.4 micron diameter PSHPs. The subcontractor instrumentally monitored the development of the spheres (both nonsilanized and silanized) before and after subsequent compressibility and viscosity testing utilizing scanning electron microscope (SEM), electron spectroscopy for chemical analysis (ESCA), and X-ray fluorescence (XRF).

Execution of this project required completion of the following sequential steps:

- Production of 0.4 micron diameter PSHPs
- Silanization of the PSHPs
- Preparation of a high-solids containing dispersion
- Viscosity analysis of the dispersion
- High temperature/high pressure compressibility testing of the dispersion
- Instrumental analyses on the spheres resulting from each of the previous steps.

Preparation of Polystyrene Plastic Spheres. Approximately ten (10) pounds of 0.35 to 0.4 micron diameter PS plastic spheres were prepared by spray drying an emulsion of uncrosslinked liquid polystyrene and aqueous base (ammonium hydroxide) into a drying chamber equipped with an ultraviolet (UV) light. By spraying the emulsion through an atomizer, the aqueous based formed microscopic spherical droplets having a surface coating of the nonmiscible polystyrene. Concurrent with droplet formation, the polymer was crosslinked by the UV light into a surface coating which was congruent with the droplet.

Preparation of PSHPs. Although microscopic examination verified the PS spheres to be structurally intact, they were known to contain the aqueous base from the spray drying process. Therefore the plastic spheres were dehydrated by heating at 80° to 90° C for a period of 48 hours. This dehydration

treatment resulted in the removal of the residual liquid and created voids in the center of the polystyrene plastic spheres (i.e., hollow plastic spheres - HPS).

The resulting HPS were then elementally analyzed and subjected to SEM for further examination. Elemental analysis determined the concentration of nitrogen-containing base that would continue to internally contaminate the spheres. SEM micrographs verified the sphere size, structural integrity, and the presence of voids.

Silanization of PSHPS. In order for PSHPS to have the greatest influence on the compressibility of hydraulic fluids, they must be intimately combined with the fluid as a concentrated suspension or dispersion. However, PSHPS are immiscible in silicone fluid and, therefore, must be chemically treated with silicon (silanization) at their surface in order to enhance the dispersion of the spheres into the fluid. The chemical used for this surface treatment of the spheres is hexamethyldisilane (HMDS).

A bench-scale laboratory procedure established the technique for chemically coating the surface of PSHPS with silyl groups. The silanization procedure required HMDS as the silanizing agent, polydimethylsilane (PS Q35) of 1 centistroke viscosity for the reaction medium and trimethylchlorosilane (TMC) as the silanizing catalyst. The reaction mixture was combined and stirred for twelve hours at 70° to 80°C. The resulting silanized product was elementally analyzed to determine the silicon concentration.

Once the silanization process was verified, the bench-scale laboratory technique was scaled up in order to provide larger quantities of silanized PSHPS. A typical batch consisted of 1000 grams of PSHPS, 5 liters of PS Q35 and 300 grams of HMDS which were placed in a 12 liter round bottomed flask fitted with an overhead stirrer, a thermometer, and a condenser. Into this mixture 30 grams of TMCS was added dropwise, providing the catalytic action necessary to enhance the silanizing reaction. Once the TMCS addition was complete, the temperature was raised to 90°C and maintained for 12 hours. At the end of the reaction period, the mixture was filtered under vacuum and the residue washed the hexane until all the residual reaction solvent (PS Q35) was removed.

Elemental analysis was performed on the batch-produced, silanized PSHPS to determine the effectiveness of this procedure for incorporating a silicon-containing coating. SEM, ESCA, and XRF analyses were also conducted to verify the structural integrity of the spheres and the completeness of the silicon coating. The silanized PSHPS resulting from these analyses were used in the preparation of the dispersion.

Preparation of PSHPS Dispersions. In order to determine the optimum concentration for the homogeneous suspension of PSHPS in the hydraulic fluid, 35%, 40%, 45%, and 50% (W/W) dispersions of silanized PSHPS in Dow Corning-200 silicone fluid (1.0 centistroke viscosity) were prepared. The process required the use of a Waring blender (for the high shear milling action) equipped with an explosion proof motor base to effectively mix the spheres with the silicone fluid into a suspension. Although four concentrations of the PSHPS dispersions were initially produced, the 40% (W/W) dispersion was determined to be the highest concentration having the properties of a true or

ideal emulsion. On microscopic examination the 40% dispersion exhibited freedom of movement of the HPS in the fluid or true "Brownian" characteristics. A Brookfield Viscometer was used to perform viscosity measurements on the 40% (W/W) dispersion and four of its dilutions (20%, 25%, 30%, and 35%). These dilutions were produced with Dow Corning 200 silicone fluid as the diluent. These viscosity determinations were conducted to characterize the working behavior of the sphere-silicone fluid dispersion.

Twenty-four pounds of the 40% (W/W) dispersion was prepared and shipped to LCWSL for further testing in the recoil systems of large caliber weapons.

Compressibility Analysis of PSHPS. In order to evaluate the ability of the 40% (W/W) dispersion of PSHPS to withstand the pressure changes and high temperatures associated with the recoil process, a preliminary compressibility analysis was also conducted. Approximately 500 milliliters of the 40% dispersion were placed into a Parr bomb (reactor) fitted with a stirrer. The reactor was heated to 180 °C and pressurized under a nitrogen atmosphere to 800 psi for five minutes. The reactor was then depressurized and after a five minute interval, repressurized to 500 psi. The depressurization was performed as slowly as possible to minimize the amount of silicone fluid escaping the reactor system. This procedure was repeated for five cycles, at which time, the reactor was brought to room temperature. The residual dispersion was removed, filtered, and the PSHPS were washed with hexane and dried for subsequent instrumental analyses. SEM and XRF were used to evaluate any changes in the element content and surface properties of the spheres.

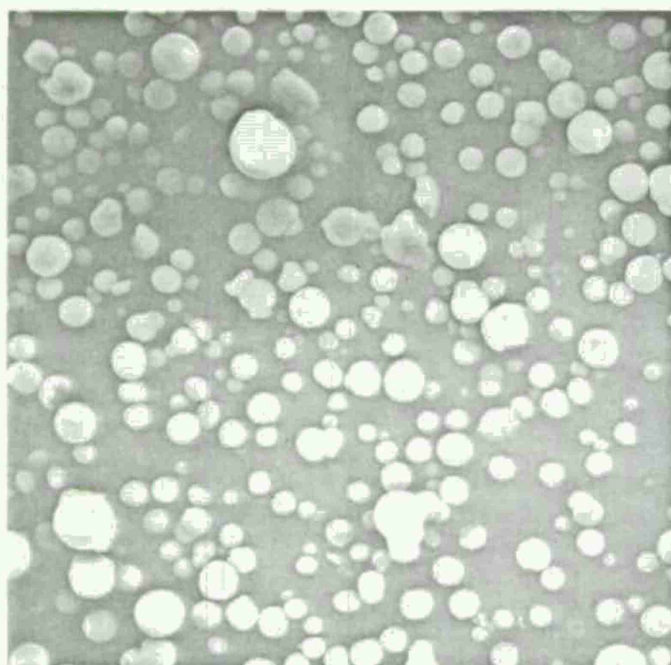
RESULTS AND DISCUSSION

The results of the instrumental laboratory analyses of PSHPS conducted during this evaluation are described below. This discussion reflects information on the production, silanization, and suspension of PSHPS and their subsequent compressibility and viscosity testing.

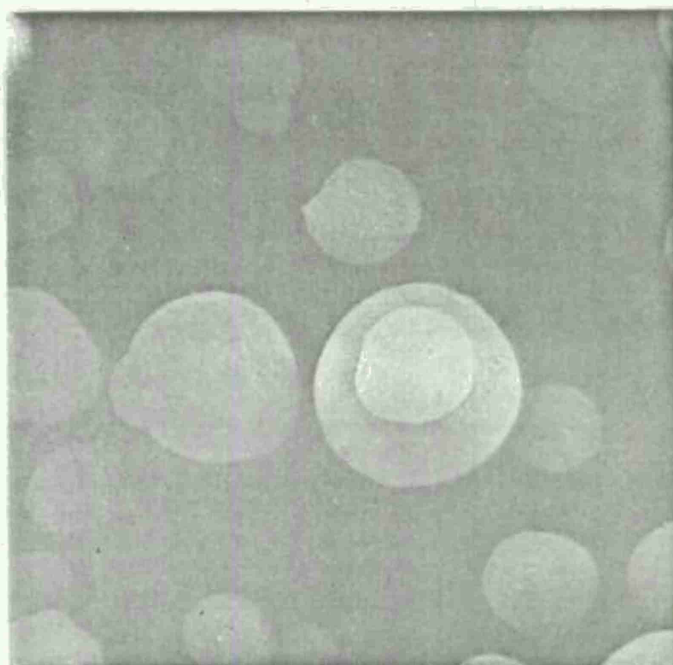
PSHPS Production. After formation and drying of the PSHPS, analysis was conducted to establish elemental concentrations and determine the degree of nitrogen-containing base contamination present in the spheres. These elemental analysis demonstrated concentrations of 77.05% carbon, 8.03% hydrogen, and only 0.21% nitrogen (the remaining element is assumed to be oxygen).

Scanning electron microscopic examination of the HPS (figure 1) revealed that the polymeric spheres formed spherical aggregates 10 to 30 microns in diameter. These aggregates were formed during the spray drying process of initial sphere production. The individual HPS comprising the spherical aggregates were found to be of uniform construction, approximately 0.35-0.4 microns in diameter and containing a central void area and having an average wall thickness of 0.1 to 0.2 microns.

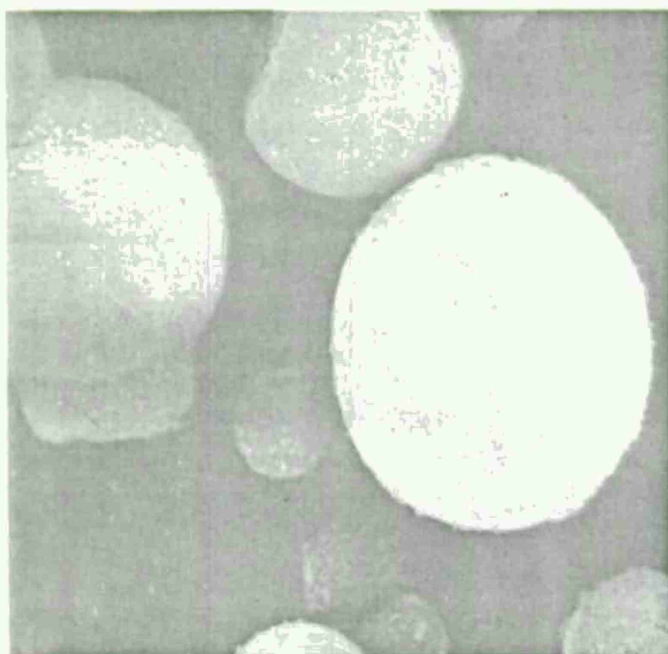
The aggregation of spheres has been previously reported in the production of HPS. A better choice of the chemical stabilizer may reduce the aggregating effects of the HPS production process. The incorporation of a stabilizer of similar volatility to that of the polymer may also reduce or eliminate sphere aggregation.



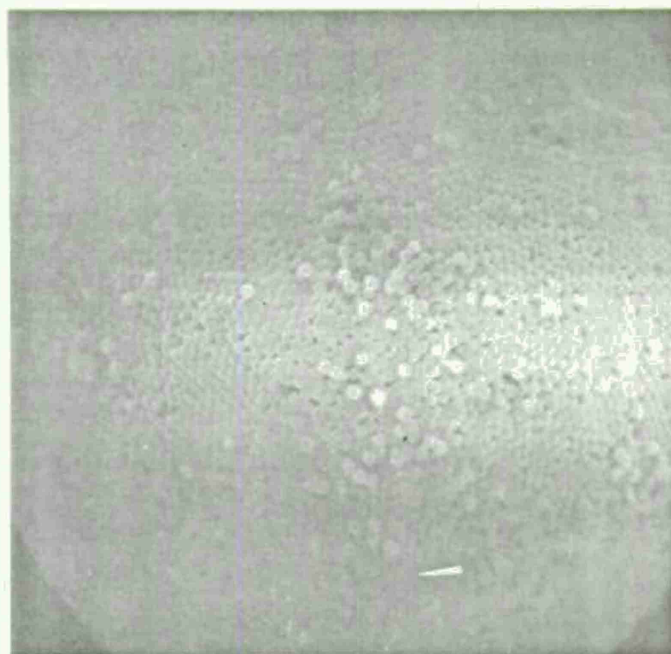
X200



X1,000



X2,000



X5,300

Figure 1. Scanning Electron Micrographs of HPS Blank.

PSHPS Silanization. Elemental analysis of the silanized PSHPS produced by the bench-scale laboratory procedure confirmed a 0.33% silicon content. This concentration indicates a successful covalent incorporation of silyl groups onto the surface of the spheres. However, the silicon content in two of three sphere samples randomly selected from the three batches produced during the scaled-up procedure were found to have a lower silicon content than the bench-scale samples. The results of these elemental analyses are given in table 1 and reflect suitable quantities of silicon incorporation for formation of the sphere-silicon fluid dispersion.

Table 1. Elemental Analysis of Silanized PSHPS

SAMPLE	%C	%H	%Si	%N
BENCH	77.05	8.03	0.33	0.21
BATCH 1	76.09	8.32	0.20	<0.1
BATCH 2	75.38	8.31	0.36	0.47
BATCH 3	75.81	8.39	0.21	<0.1

An analysis of the treated PSHPS by XRF was used to determine the content of silicon relative to other elements present. The XRF data (figure 2) indicate silicon is contained in the sample. The results of the XRF analysis support the elemental analysis of silanized HPS also indicates that silicone exists in association with the spheres.

The batch produced silanized PSHPS were also examined by SEM (figure 3). Comparison of figures 1 and 3 reveal that the structure of the silicon treated spheres is identical to the untreated spheres. It is, therefore, unclear from these micrographs if the silanization was continuous for each individual sphere or if the silanization process results in a silicon coating for the mass or aggregation of spheres as a whole. Additionally, these SEM micrographs (figure 3) do not indicate any apparent structural damage to the sphere walls and the voids remain intact.

ESCA was used to evaluate silicone "enrichment" on the surface of the silane-treated HPS. ESCA techniques establish elemental concentrations to an effective sampling depth of approximately 50 Angstroms within an organic matrix. As indicated by the data chart presented in figure 4, silicon was not detected by this procedure. The absence of silicon in the surface layers of the HPS samples used in this analysis suggests that all spheres may not be coated by the silanization process or that the silanization treatment may not be restricted to the sphere's surface.

PSHPS Dispersion Formation. Microscopic examination was to determine the optimal concentration of the PSHPS/fluid dispersion. Observation revealed free movement of the HPS in the 40% (W/W) dispersion and thus, indicated that maximum viscosity (weight percent of PSHPS to silicone fluid) which retained its stability to separation. Although the 35% dispersion was stable and

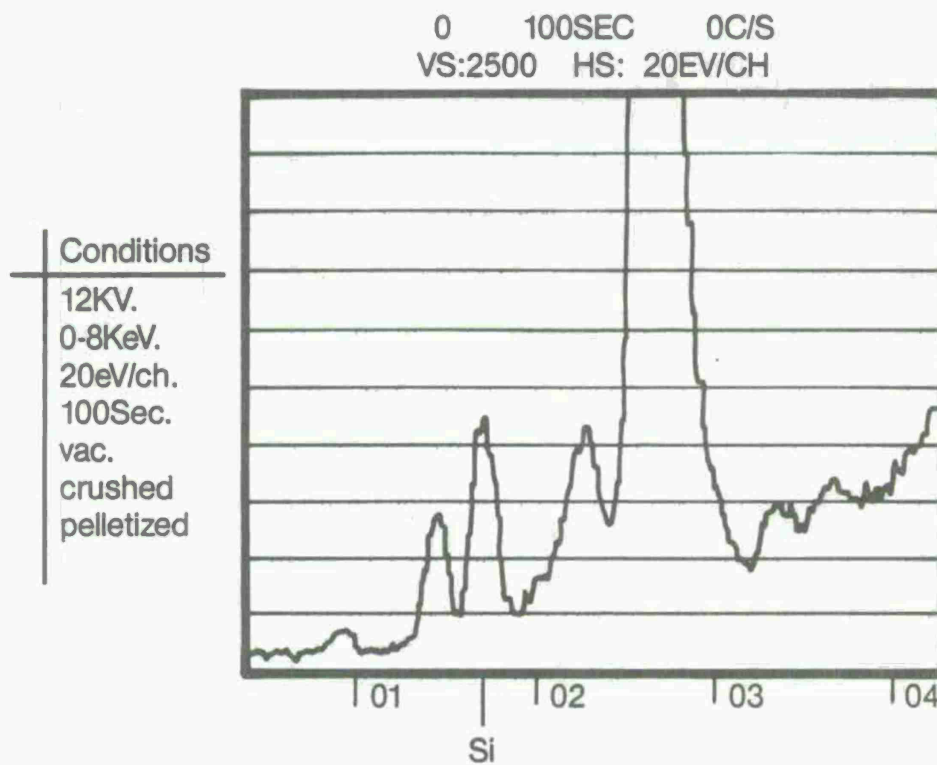
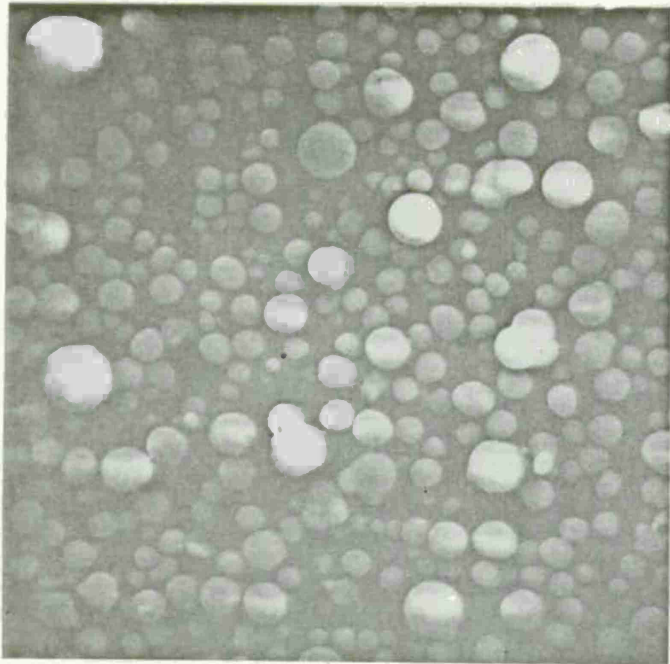
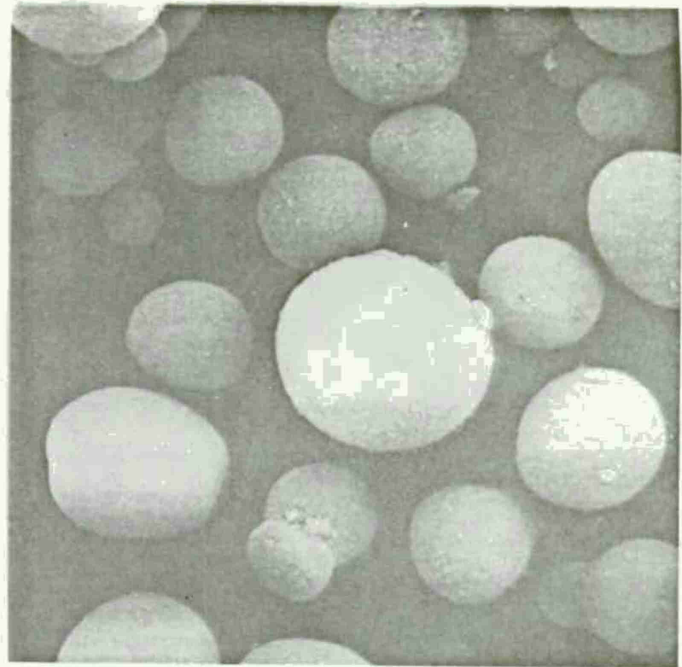


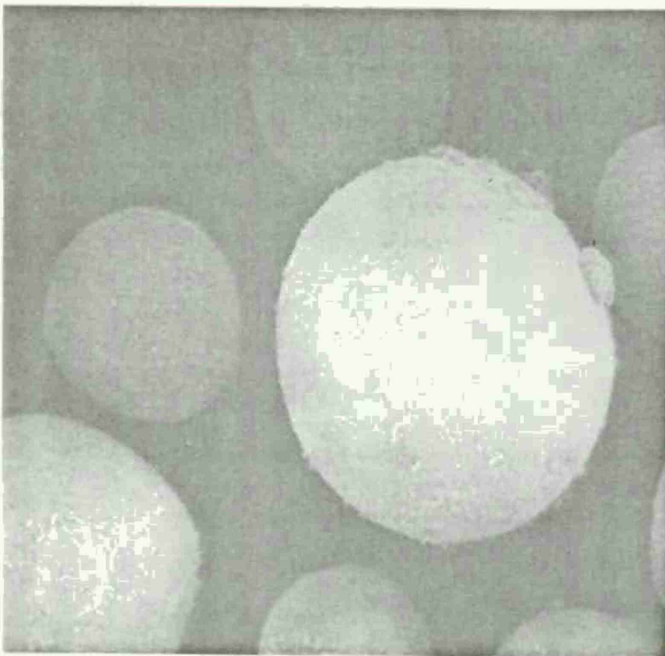
Figure 2. X-Ray Fluorescence Data for Silane Treated Hollow Plastic Spheres.



X200



X1,000



X2,000



X5,300

Figure 3. Scanning Electron Micrographs of Silane Treated HPS.

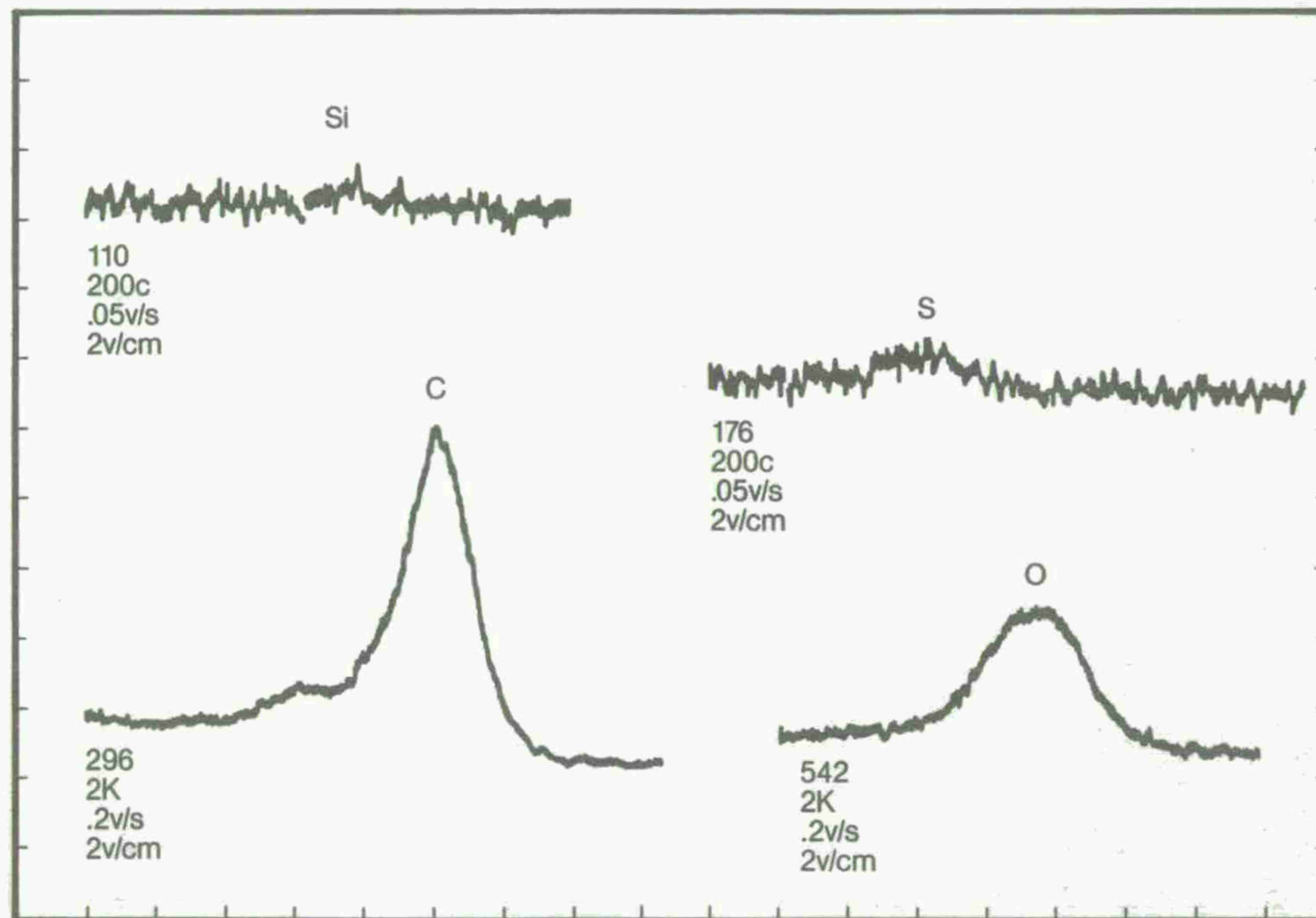


Figure 4. ESCA Data for Silane Treated Hollow Plastic Spheres.

exhibited true emulsion qualities, the 40% dispersion exhibited these qualities while reflecting a higher phase concentration. The 50% dispersion, however, was much too concentrated to maintain its emulsion stability. It can be concluded, therefore, that the 40% (W/W) dispersion of PSHPs in silicone fluid was a true emulsion and offered the best work viscosity for this analysis.

Viscosity Measurements of 40% (W/W) PSHPs Dispersion. Viscosity measurements of the 40% (W/W) PSHPs dispersion along with appropriate dilutions (20%, 25%, 30%, and 35%) were determined to characterize the behavior of this emulsion. The resulting data is presented in table 2 and plotted in figure 5.

Table 2. Viscosities of PSHPs Dispersions

Sample No.	% Solids	RPM	Spindle No.	Scale Reading	Factor	Viscosity cps
1	40	60	2	33	5	165
2	35	60	1	63	1	63
3	30	60	1	31	1	31
4	25	60	1	14	1	14
5	20	60	1	8	1	8

NOTE: Stock dispersion 40% (W/W). Samples 2-5 were prepared by diluting the stock dispersion with Dow Corning 200 (1 Cstk) silicon fluid.

An ideal emulsion behavior is depicted for these dispersions. Initially, as the solid content increases (0 to 20% spheres), the viscosity change is small. However, at higher solids content (20 to 40% spheres) the viscosity increases significantly. At lower concentrations the available space in the fluid for sphere displacement is quite abundant however, as higher concentrations of solids are attained in the limited fluid environment, the viscosity increases rapidly.

Instrumental Analyses After Compressibility Testing. SEM and XRF analyses were conducted on the 40% (W/W) PSHPs dispersion in order to determine the effects of compressibility testing in simulating the elevated pressures and temperatures that result during the recoil portion of the weapon firing process. SEM was utilized to identify any structural damage to spheres that resulted from the compressibility tests (figure 6). The structure of a small percentage (<10%) of the sphere aggregates appeared to have deformed or become elliptical under the compressibility test conditions. The remaining aggregates appear structurally undamaged. The spheres comprising these aggregates were unchanged in diameter and retained their central voids. It was noted, however, that the majority of the aggregates were no longer covered by a smooth, continuous layer of spheres as illustrated in figures 1 and 3. The increased roughness in the outer layers of the aggregates suggests that some of the spheres forming the outside layers had either been lost from the

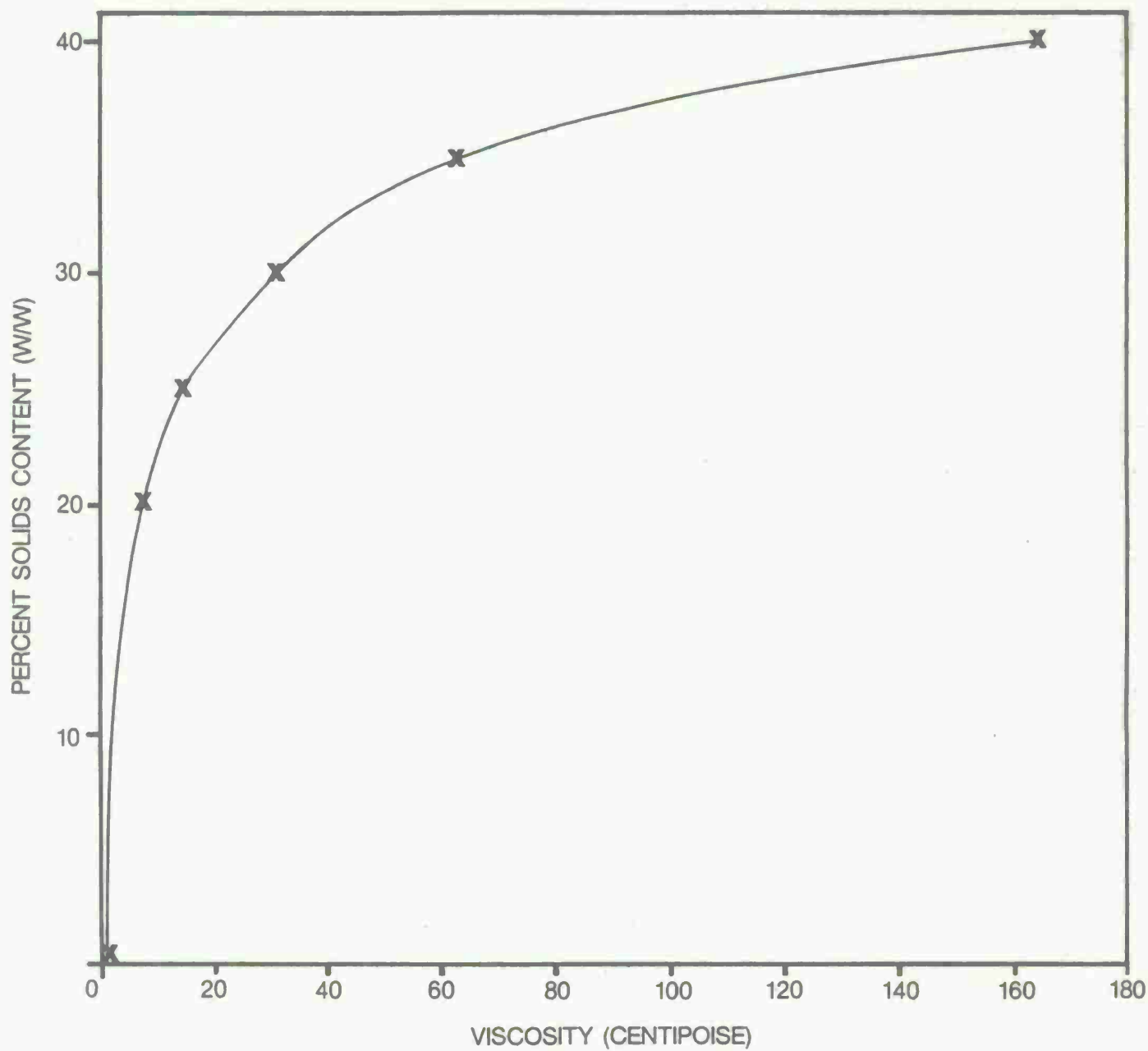
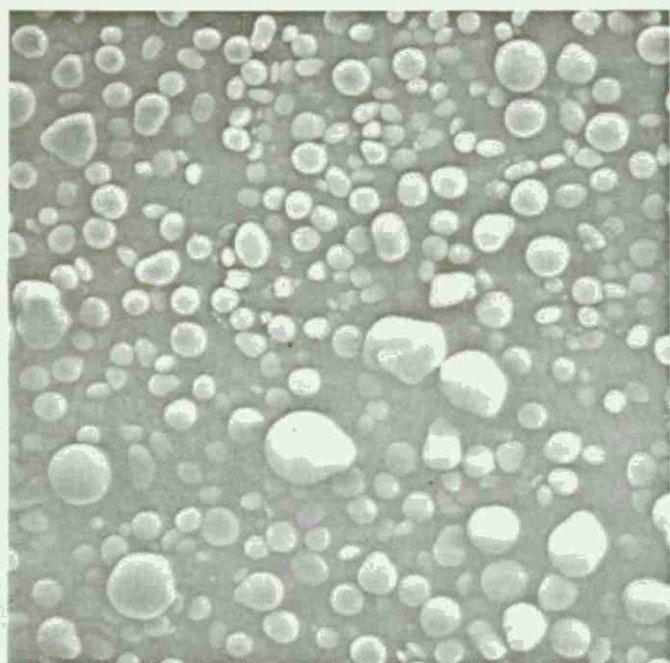
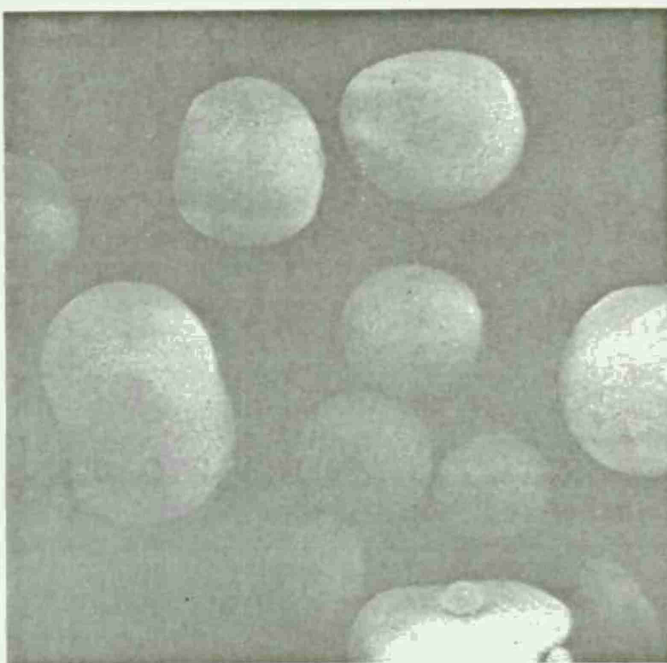


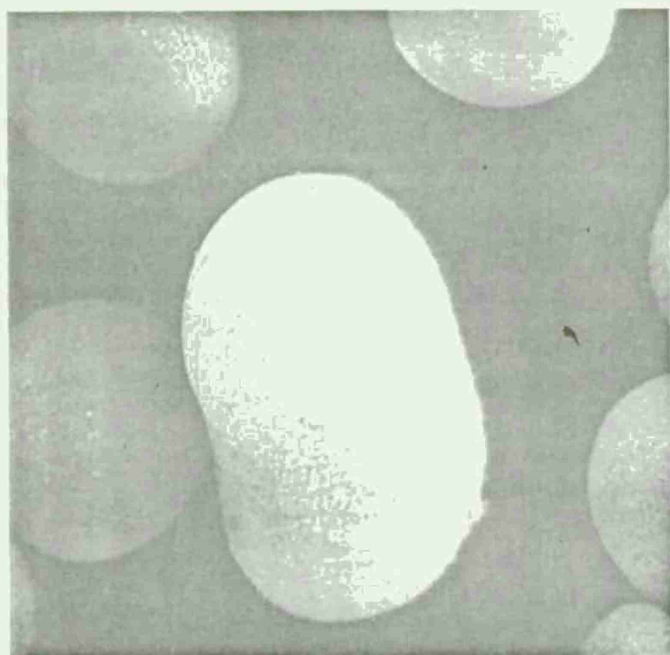
Figure 5. Comparative Viscosities of PSHPS Dispersions.



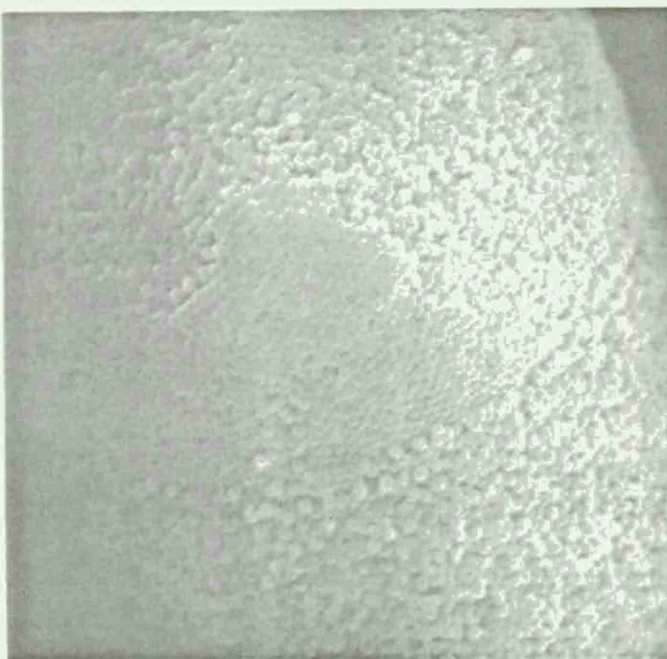
X200



X1,000



X2,000



X5,300

Figure 6. Scanning Electron Micrographs of HPS After High Pressure/High Temperature Treatment.

aggregate mass or were forced into the aggregate of spheres by the extreme conditions of the test.

Since the SEM micrographs did not demonstrate any loss or any "sluffing off" of the very thin silicon-containing coat, an XRF analysis was also conducted on a sample of the compressibility tested PSHPs. The results of the XRF scan presented in figure 7 indicate a much lower concentration of silicon. This reduction in the silicon concentration of the PSHPs after compressibility testing may be due to:

- the severe conditions of the test causing some loss of the silicon-containing coat.
- the drying of some spheres due to the loss of silicone fluid during the testing.
- the sample used for the XRF analysis is a non-representative sample of the tested spheres.

CONCLUSIONS

Experimental results and test data indicate that through the techniques used in this study, a silicon coating was successfully applied to aggregates of PSHPs. In addition, a successful technique for the production of a 40% (W/W) dispersion in Dow Corning 200 silicone fluid was demonstrated. The high temperature, high pressure compressibility test data indicates that a stable dispersion has been produced which can withstand the environment associated with the pressures specified in this study (800 psi).

A 40% (W/W) dispersion of silanized PSHPs was produced. This dispersion was shown to exhibit ideal emulsion behavior by viscosity measurements indicating the 40% (W/W) dispersion to be a stable mixture. The individual spheres were found to be 0.35 - 0.4 microns in diameter with a wall thickness of approximately 0.1 micron. Relating these measurements of sphere size to the calculated parameters for HPS given in CSC-EL's polyurethane feasibility report, a radius ratio ($A = \text{inside sphere radius} / \text{outside sphere radius}$) of 0.65 to 0.85 is obtained. According to the simplified compressible model as illustrated in figure 8, this yields a compressibility of the PSHPs of about 2.2 to 6.5% in volume.

The PSHPs were formed as aggregates of spheres 10 to 30 microns in diameter, rather than individual units. Although these spheres aggregates are expected to enhance hydraulic fluid compressibility, their efficiency of reaction could limit proper silicon coating, dispersion formation and ultimately, polymer-hydraulic fluid compressibility. Study results fail to clarify whether the silanization process was effective in coating the individual spheres versus the sphere aggregations, and the total impact of sphere aggregates on the compressibility characteristics of the fluid suspension. Aggregation during microsphere production may be minimized or eliminated by incorporating a proper stabilizing agent during sphere formation and additional study should be made to determine and evaluate the methods to minimize this aggregating phenomenon.

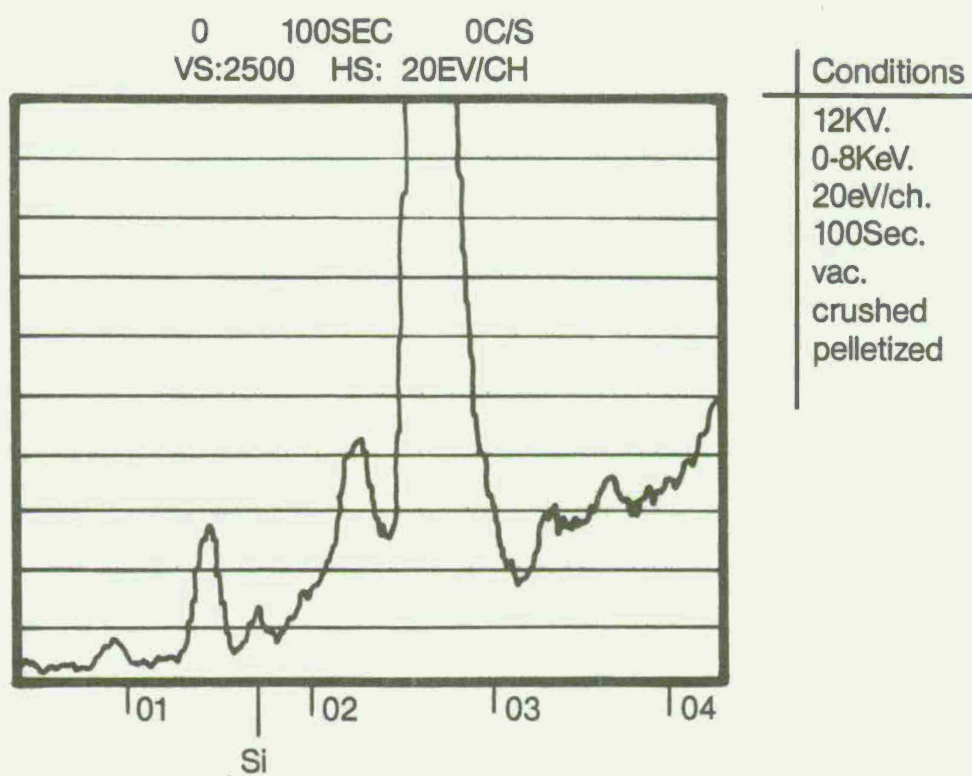


Figure 7. X-Ray Fluorescence Data for PSHPS After High Pressure/High Temperature Compressibility Testing.

$$A = \frac{\text{inside radius}}{\text{outside radius}}$$

↑
Thinner Wall

↓
Thicker Wall

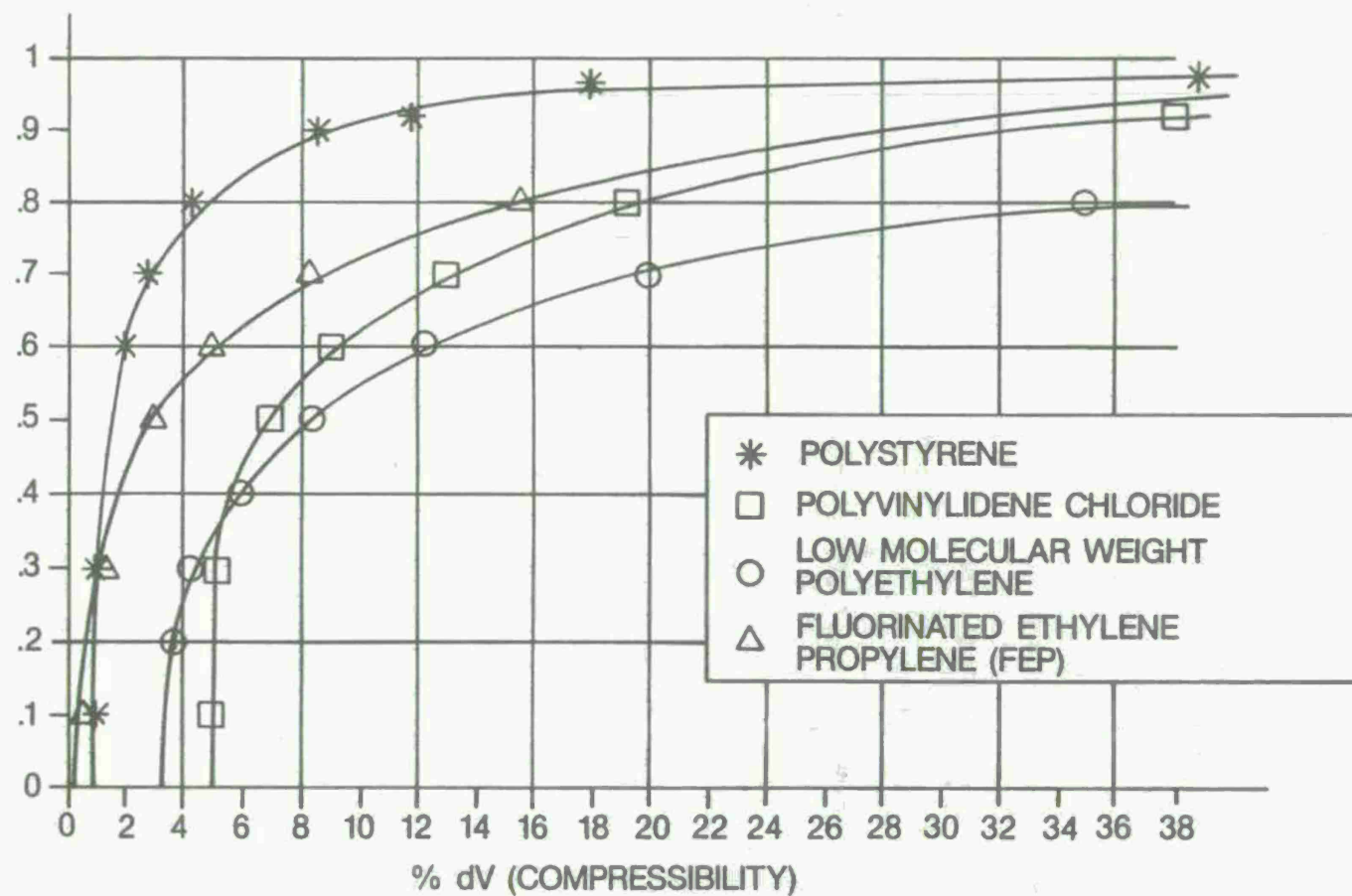


Figure 8. Calculated Compressibility as a Function of Wall Thickness.

The conditions of bulk compressibility testing (i.e., a temperature of 180°C (356°F) and pressures of 500 and 800 psi) were harsh enough to establish the durability of the spheres in a severe environment. However, the pressurization/depressurization cycle utilized in this test process required a minimum of ten minutes, and did not realistically simulate the frequency of elevated temperatures and pressures that will occur during the recoil phase of the firing process. A testing system of better design than the Parr bomb should also have been utilized to eliminate escaping silicone fluid during depressurization.

Although the PSHPS were considered to be highly crystalline and, therefore, brittle, their ability to tolerate the compressibility test pressures does indicate an amorphous character not previously expected. This quality of the PSHPS could allow even thinner walled spheres to be produced which should possess an even greater degree of compressibility.

Elemental and instrumental analyses support the production of a proper PSHPS dispersion for use in the recoil systems of large caliber weapons.

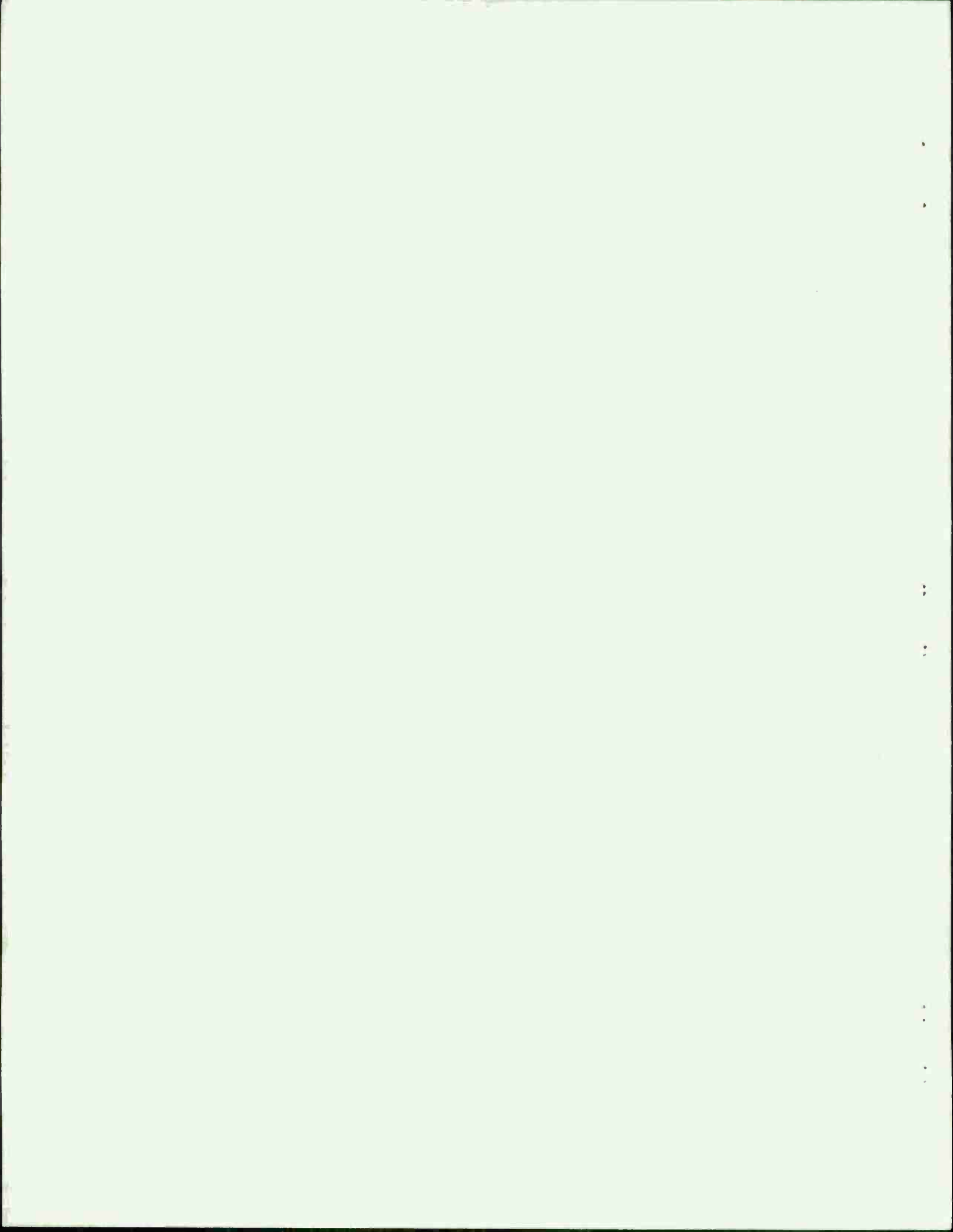
RECOMMENDATIONS

Although the preliminary bulk compressibility testing and instrumental results indicate that the 40% (W/W) dispersion of PSHPS can be used to enhance hydraulic silicone fluid compressibility, further bulk compressibility testing under dynamic conditions are necessary. The following tasks are recommended as a follow-on to the current effort:

- Additional bulk compressibility testing be performed at temperatures and pressures that simulate the real-world conditions of a weapon recoil process (i.e., temperatures greater than 200°C and pressures of 1000 to 5000 psi).
- Investigate methods of maximizing the formation of independent spheres and minimizing the formation of the sphere aggregates that resulted from the technique used in this study.
- Explore the utilization of more amorphous polymers (such as fluorinated ethylene propylene (a Teflon) and polyvinylidene fluoride) as microspheres.
- The potential use of polymeric powders to increase the compressibility of hydraulic fluids should also be investigated.

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APPENDIX

FINAL REPORT OF
ROHM AND HAAS COMPANY

Dr. Dilip M. Nene

BACKGROUND

Rohm and Haas learned of the need for a compressible fluid for an improved artillery recoil mechanism from the talk given by Mr. Vincent Chin of ARRADCOM at the Advanced Planning Briefing for Industry at West Point on 26 September 1978. The concept for developing a compressible fluid based on hollow plastic spheres (HPS) was developed at Rohm and Haas and initial calculations reported by Dr. Martin Vogel on 15 August 1979 indicated that this approach was possible. Considerable internal work was done to develop a procedure to provide a stable suspension of HPS in silicon fluid. On 21 April 1980, an unsolicited proposal containing the Rohm and Haas idea, the calculations, and information on initial suspensions of HPS in silicon fluid was submitted to ARRADCOM. This proposal was assigned registration number UN 078-80.

A presentation was made on that proposal to Mr. Walter Pope of ARRADCOM on 14 May 1980. Discussions continued on this idea with ARRADCOM through 1980 and 1981. On 2 December 1981, Mr. Robert Dombroski of ARRADCOM and Paul Fassnacht and James Kotter of Computer Science Corporation visited Rohm and Haas to discuss this proposal. These discussions resulted in the receipt of a Purchase Order Number 00328s from Computer Sciences Corporation to prepare a sample of HPS in silicon fluid. This sample is to be used to test the practicality of the Rohm and Haas HPS compressible fluid concept.

INTRODUCTION

The hollow plastic spheres were obtained by spray drying an emulsion (E-1978). The spray drying was done in the Semi-Works at our Philadelphia plant. The spheres thus obtained were found to be intact (no structural damage seen) and contained ammonia in the voids. The HPS were then heat treated at about 80°C-90°C for 48 hours. The treatment results in the removal of ammonia from the voids without damaging the spheres. These spheres were then analyzed for the %C, %H and %N. The elemental analysis was as follows:

$$C = 77.05, H = 8.03, N = 0.21$$

On examination of the HPS it was found that these were in form of aggregates, the outer diameter of which range from 10 microns to 30 microns. These aggregates were formed during the process of spray drying and the size of the aggregates was defined by the size of the emulsion drops created by the atomizer. Nevertheless, the individual particle were found to be approximately 0.4 microns. In the future as the need be we will use the available in-house expertise, that will allow us to considerably reduce the process of aggregation of the HPS during spray drying.

MATERIAL DATA

- | | |
|--|--|
| 1. Polydimethylsiloxane
(PS 035) 1 Cstk | Petrarch Systems
2731 Bertram Road
Bristol, PA 19007 |
| 2. Hexamethyldisilazane
HMDS | " |
| 3. Trimethylchlorosilane
TMCS | " |
| 4. Dow Corning-200
1 Cstk | Dow Corning
Michigan |

EXPERIMENTAL DETAILS

Several sets of experiments were conducted and are listed in their chronological order.

- A. Approximately 10g of HPS were suspended in 60 mls of PS 035 (1 Cstk) and 6g of HMDS. We also had available PS 038 (5 Cstk) and PS 039 (10 Cstk); two additional reaction mixtures were made using these fluids. All of the reaction mixtures were placed in glass jars and shaken overnight at room temperature.

Another similar set of reaction mixtures was made, but this time the mixtures were shaken for 48 hours at room temperature.

At the end of each time period the mixtures were filtered, the residues washed with hexanes and dried in a vacuum oven at about 80°C to 90°C. The dried samples were analyzed for %C, %H, %N and % Si. The analytical data is included in Table I. The analytical data indicated that we were not getting any significant amounts of Si incorporation.

- B. After the initial experiments as described in Section A, it was decided to run the experiments in round bottom flasks using overhead stirrers, using hexanes as a reaction medium rather than PS 035.

Reactions using the following compositions were conducted:

- 1) HPS + PS 035 + HMDS for 96 hrs at room temperature
Product ID = 1D, % Si = 0.20
- 2) HPS + Hexanes + HMDS + TMCS
At room temperature for 12 hrs and then at 70°C to 80°C for about 4 hours.
Product ID = 1F, % Si = 0.06
- 3) HPS + HMDS + PS 035
At 75°C to 80°C for 12 hrs
Product ID = 1E, % Si = 0.33
- 4) HPS + HMDS + Hexanes + TMCS
At 70°C for 12 hrs
Product ID = 1F, % Si = 0.06

Based on the % Si analysis, it was decided to use PS 035 as a medium of reaction and also to run the reaction at an elevated temperature. It was also recognized that the products 1D and 1E contained 0.2% and 0.33% Si resp. in contrast to products 1A through 10B wherein the % Si was found to be from 0.06% to 0.09%. These results indicated that we now had a successful method of coating the spheres with Silyl groups.

SCALE UP

Several large batches were run in order to prepare the required amounts of dry, silicon coated HPS.

In a typical batch, 1000 g of HPS, 5 litres of PS 035 and 300 g of HMDS were placed in a 12 liter round bottom flask fitted with an overhead stirrer, a thermometer attached to a thermowatch, and a condensor. Into this mixture was added a 30 g of TMCS dropwise. Once the addition was complete the temperature was raised to and maintained at 90°C for about 12 hrs. At the end of the reaction, the mixture was filtered under vacuum and the residue was washed with hexanes until all the residual solvent was removed. A small sample was carefully dried and the bulk material was used as is in the preparation of the dispersions.

Three randomly picked analytical samples (from three different batches) were submitted for elemental analysis. The samples were designated 1H, 1K, and 1L. The results are included in Table II.

The product thus prepared was examined for the voids and also for, if any, structural damage. The examination indicated that there was no significant amount of damage and the voids were still intact.

PREPARATION OF DISPERSION

In a Waring blender, using an explosion-proof motor base, dispersions containing 35%, 40%, 45%, 50% solids (W/W) in Dow Corning-200 (1 Cstk) fluids were made. These dispersions were examined and it was found that the 40% solids containing samples showed true "Brownian" characteristics. As a result of this data we chose to prepare 40% (W/W) dispersion. In a manner described earlier 24 lbs of 40% (W/W) dispersion was made and shipped to Dover, NJ. Also about 1 litre of the suspension was shipped to TRW in California for compressibility analysis.

HIGH PRESSURE TREATMENT

Approximately 500 mls of the dispersion was subjected to high pressure and temperature. The experiment was done as follows: In a Parr bomb fitted with a stirrer was placed 500 mls of the dispersion. The bomb was heated to 180°C and pressurized by N₂ to 800 psi for 5 minutes. During this time some vapors were seen leaking from the bottom of the reactor. The reactor was then depressurized and after a 5 minute interval repressurized to 500 psi. This procedure was repeated through 5 cycles. At the end of 5 cycles, the reactor was brought to room temperature, the residual dispersion removed, filtered, washed with hexane and dried. The residue appeared to have acquired a slight tan coloration. The product thus obtained was checked for voids. An estimated 90% of the spheres were intact.

VISCOSITY OF THE ORIGINAL SUSPENSION AS USED AS AT SEVERAL DILUTIONS

The viscosities were measured on Brookfield viscometer. The data is included in Table III.

SCM AND ESCA ANALYSIS

The HPS were analyzed SCM and ESCA for their surface properties. The analysis was done on HPS before and after silylation and also on HPS which were subjected to high temperature and pressure conditions.

The analysis indicates that the spheres were unaltered or damaged by the silylation process, furthermore the voids within the spheres were intact. The analysis of the HPS subjected to high temperatures and pressure indicate that although a small percentage of spheres have become elliptical, they are structurally undamaged and still retain the voids.

CONCLUSIONS

All the experimental results and the test data indicate that we have been very successful in coating the spheres with silicon as well as making a 40% (W/W) dispersion in Dow-Corning 200 silicon fluid. The high temperature, high pressure data indicates that we have made a stable dispersion which we feel can withstand reasonably high pressures.

TABLE I

<u>Sample ID</u>	<u>% C</u>	<u>% H</u>	<u>% Si</u>	<u>% N</u>
HPS(0)	77.1	8.0	-	0.21
1A	76.9	8.0	0.09	0.22
5A	76.7	8.1	0.08	0.20
10A	76.5	8.0	0.07	0.25
1B	76.9	8.0	0.07	0.23
5B	76.9	8.1	0.06	0.34
10B	77.1	8.1	0.07	0.22

A = Reaction mixutres shaken for 12 hrs.

B = Reaction mixtures shaken for 48 hrs.

1,5, 10 represent the viscosity in Cstk of polydimethyl-siloxanes.

HPS(O) = Original, unsilylated HPS

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TABLE II

<u>Sample ID</u>	<u>% C</u>	<u>% H</u>	<u>% Si</u>	<u>% N</u>
1D	-	-	0.20	-
1E	-	-	0.33	-
1F	-	-	0.06	-
1G	-	-	0.07	-
1H	76.09	8.32	0.20	<0.1
1K	75.38	8.31	0.36	0.47
1L	75.81	8.39	0.21	<0.1

1D, 1E, 1F, 1G were analyzed only for Si.

1K - Although shows 0.36% Si, it also shows 0.47% N. This indicates that the sample probably still contains residual HMDS.

TABLE III

Viscosity by Brookfield Viscometer

<u>Sample No.</u>	<u>% Solids</u>	<u>RPM</u>	<u>Spindle #</u>	<u>Scale Reading</u>	<u>Factor</u>	<u>Viscosity cps</u>
1	40	60	2	33	5	165
2	35	60	1	63	1	63
3	30	60	1	31	1	31
4	25	60	1	14	1	14
5	20	60	1	8	1	8

A. Stock dispersion 40% (W/W)

B. Samples 2-5 were prepared by diluting the stock dispersion with Dow Corning 200 (1 Cstk) fluid.

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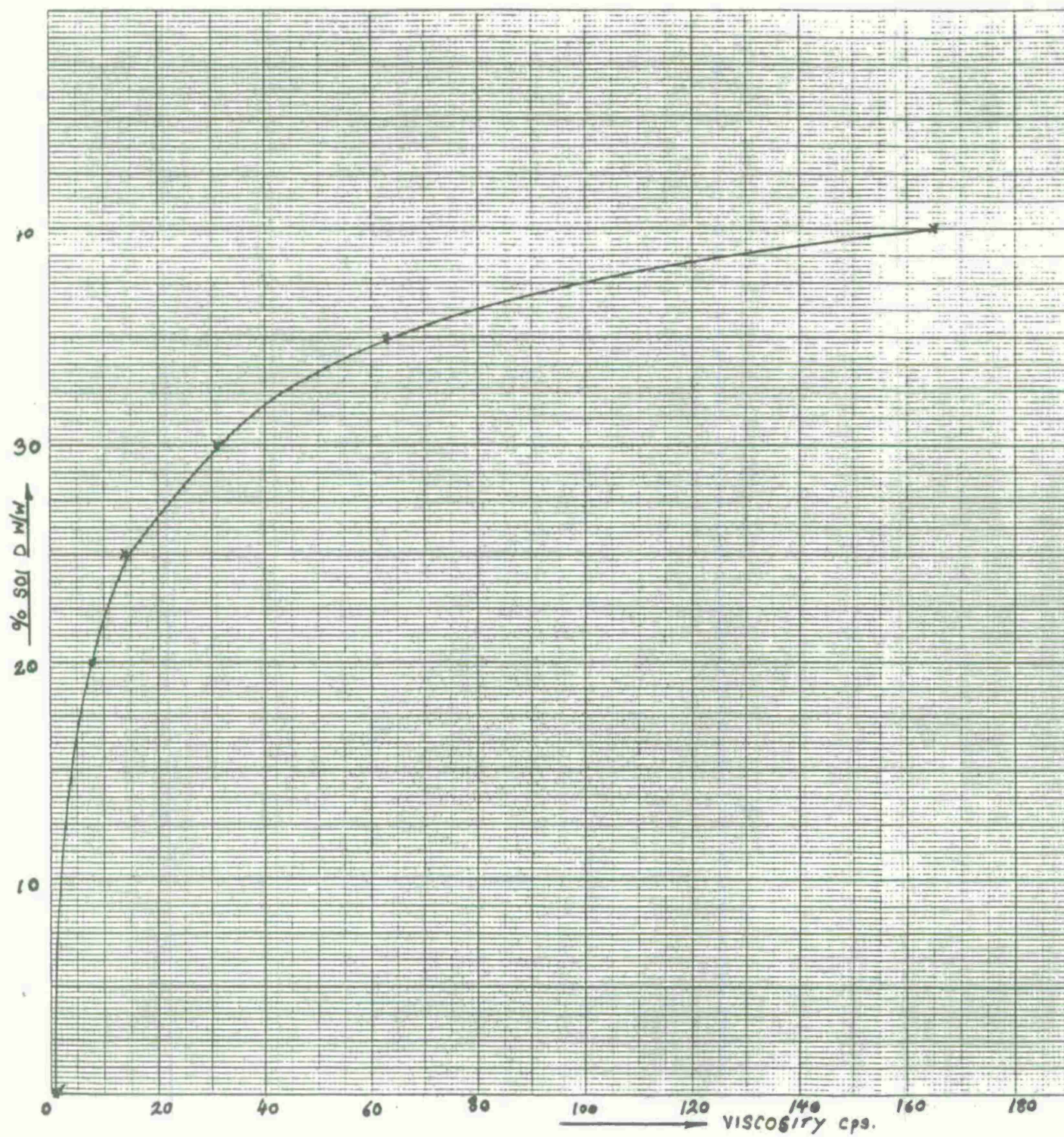
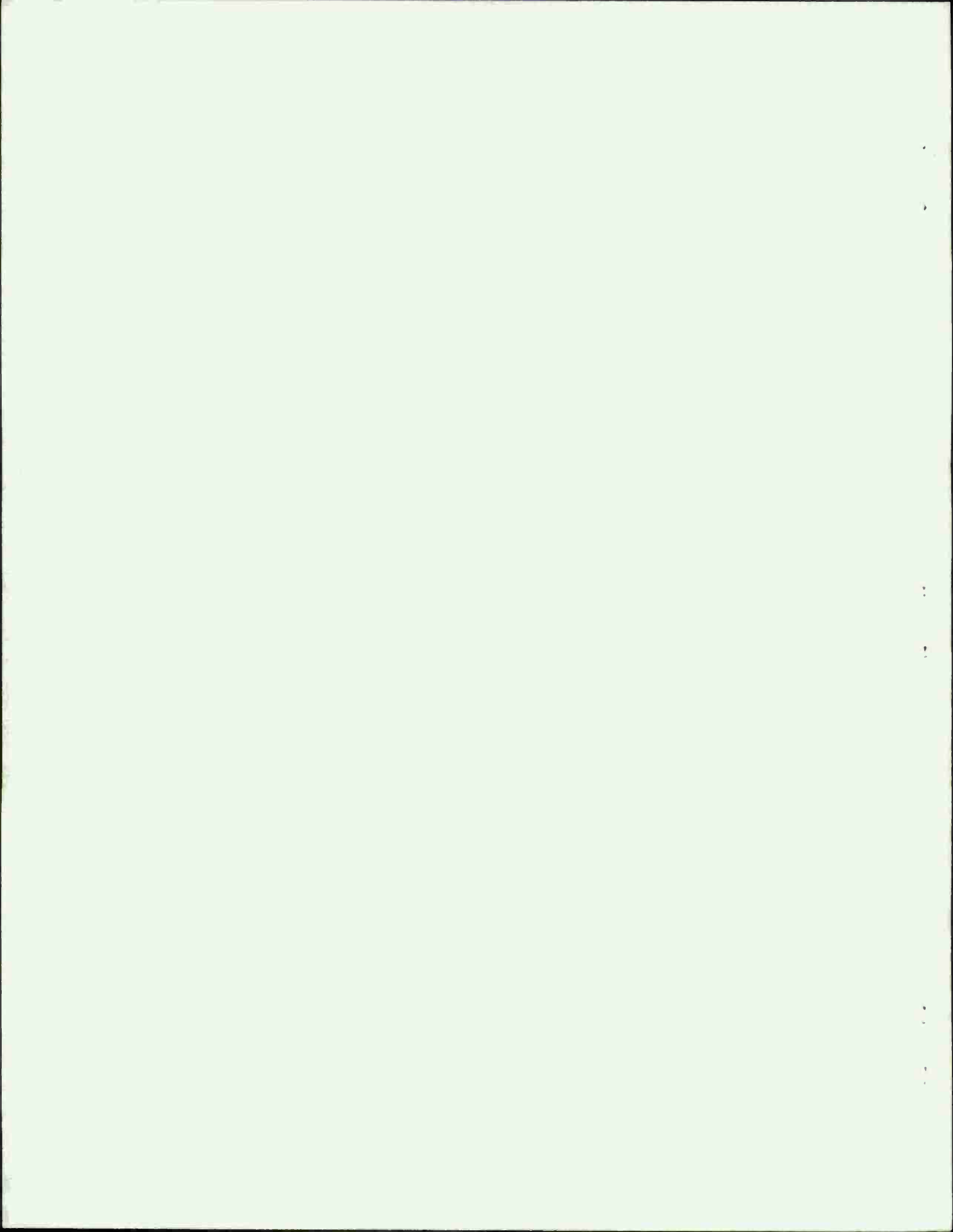


Figure 1. Graph of fluid viscosity (cps) versus percent solubility for Al-methyl siloxane



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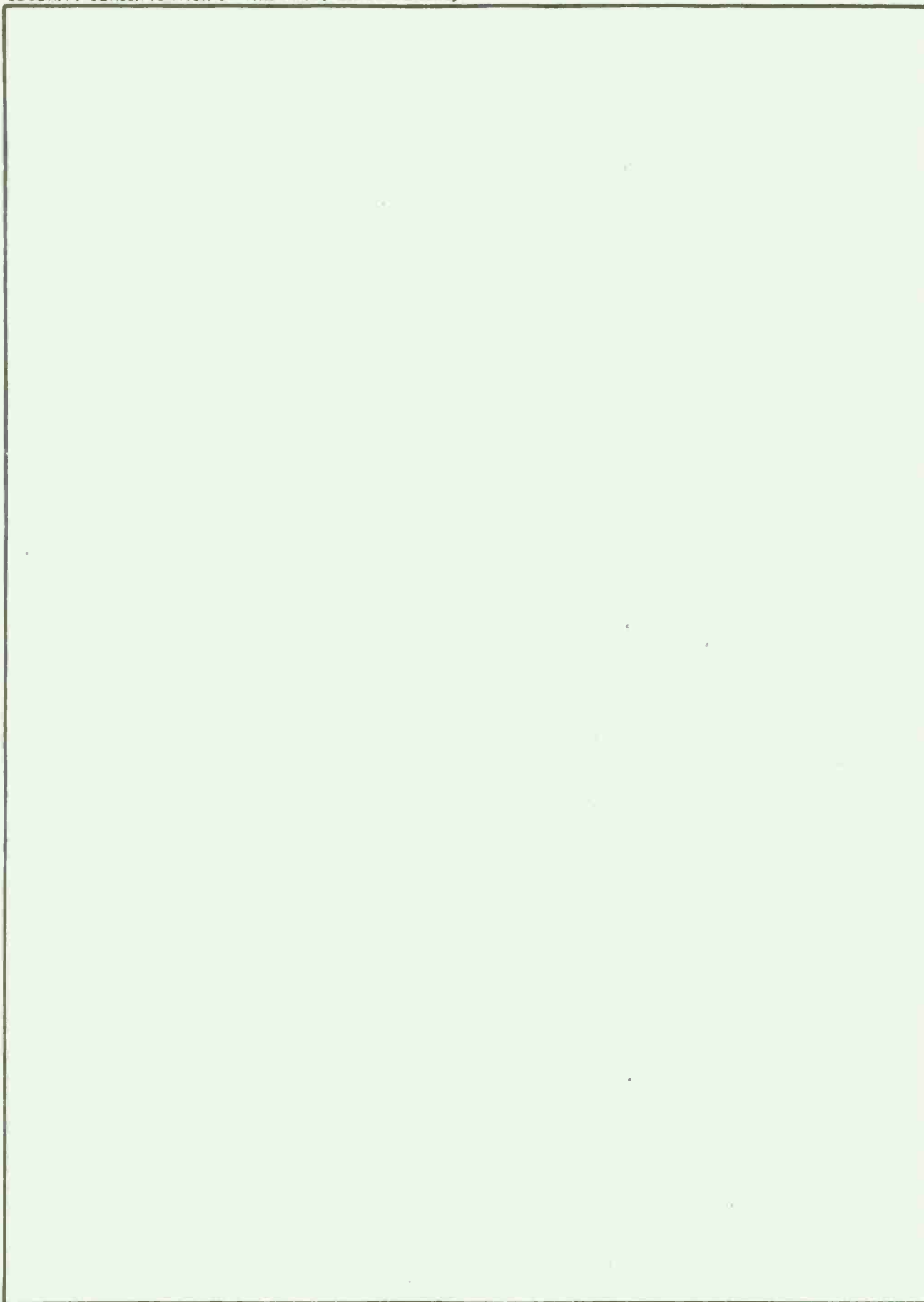
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