UNCLASSIFIED

AD NUMBER

ADB230047

NEW LIMITATION CHANGE

TO

Approved for public release, distribution unlimited

FROM

Distribution authorized to U.S. Gov't. agencies only; Specific Authority; 9 Oct 97. Other requests shall be referred to U.S. Army Medical Research and Materiel Command, Fort Detrick, MD 21702-5012.

AUTHORITY

USAMRMC ltr, 4 Dec 2002

THIS PAGE IS UNCLASSIFIED

AD_____

CONTRACT NUMBER DAMD17-97-C-7017

TITLE: Highly Destructive Polymer-Contained Neutralizing Skin Protectants

PRINCIPAL INVESTIGATOR: Dwight D. Back, Ph.D.; Meyer, John A.; Ramos, Charlie

CONTRACTING ORGANIZATION: Mainstream Engineering Corporation
Rockledge, Florida 32955

REPORT DATE: June 1997

TYPE OF REPORT: Final, Phase I

PREPARED FOR: U.S. Army Medical Research and Materiel Command
Fort Detrick, Maryland 21702-5012

9 OCT 1997

DISTRIBUTION STATEMENT: Distribution authorized to U.S. Government agencies only (specific authority). Other requests for this document shall be referred to U.S. Army Medical Research and Materiel Command, 504 Scott Street, Fort Detrick, Maryland 21702-5012.

The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision unless so designated by other documentation.

19971008 089

DTIC QUALITY INSPECTED 3

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	June 1997	Final, Phase I (22 Nov 96 - 21 May 97)

4. TITLE AND SUBTITLE

Highly Destructive Polymer-Contained Neutralizing Skin Protectants

5. FUNDING NUMBERS

DAMD17-97-C-7017

6. AUTHOR(S)

Back, Dwight D., Ph.D. , Meyer, John A., Ramos, Charlie

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Mainstream Engineering Corporation
Rockledge, Florida 32955

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U.S. Army Medical Research and Materiel Command
Fort Detrick, Maryland 21702-5012

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT

Distribution authorized to U.S. Government agencies only (specific authority). Other requests for this document shall be referred to U.S. Army Medical Research and Materiel Command, Fort Detrick, Maryland 21702-5012.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

The Phase I effort selected a small subset of novel metal alloys to be used as barriers or neutralizing agents in chemical warfare (CW) agent skin protectants. All of these substrates, prepared by our patent-pending process, were found to neutralize or immobilize both G and HD simulants when coated with an organic compound derived by reaction with a polymer or monomer. Our Phase I experiments have identified and proved out the feasibility of at least 3 metal substrates which are effective neutralizing agents toward CW agent simulants dimethyl methylphosphonate (DMMP) and 2,2'-thiodiethanol (TDE). These alloys can be oxidative, reductive, or catalytic depending on the preparation method and specific metals involved. Based on our findings, there are several more potentially effective alloys which could have similar or better neutralizing capabilities.

14. SUBJECT TERMS

skin protectant, nerve gas, mustard gas, topical protectant, hydride, metal oxide.

15. NUMBER OF PAGES

131

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	Limited

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18 298-102

USAPPC V1.00

FOREWORD

Opinions, interpretations, conclusions and recommendations are those of the author and are not necessarily endorsed by the U.S. Army.

____ Where copyrighted material is quoted, permission has been obtained to use such material.

____ Where material from documents designated for limited distribution is quoted, permission has been obtained to use the material.

DB Citations of commercial organizations and trade names in this report do not constitute an official Department of Army endorsement or approval of the products or services of these organizations.

____ In conducting research using animals, the investigator(s) adhered to the "Guide for the Care and Use of Laboratory Animals," prepared by the Committee on Care and use of Laboratory Animals of the Institute of Laboratory Resources, national Research Council (NIH Publication No. 86-23, Revised 1985).

____ For the protection of human subjects, the investigator(s) adhered to policies of applicable Federal Law 45 CFR 46.

____ In conducting research utilizing recombinant DNA technology, the investigator(s) adhered to current guidelines promulgated by the National Institutes of Health.

____ In the conduct of research utilizing recombinant DNA, the investigator(s) adhered to the NIH Guidelines for Research Involving Recombinant DNA Molecules.

____ In the conduct of research involving hazardous organisms, the investigator(s) adhered to the CDC-NIH Guide for Biosafety in Microbiological and Biomedical Laboratories.

PI - Signature 6/12/97 Date

TABLE OF CONTENTS

FRONT COVER 1

REPORT DOCUMENTATION PAGE (SF 298) 2

FOREWORD 3

TABLE OF CONTENTS 4

INTRODUCTION 5

- Subject 5
- Purpose 5
- Scope 5
- Background of Previous Work 6

EXPERIMENTAL METHODS AND MATERIALS 9

- Metal Alloy Preparation and Activation 9
- Reactions of Activated Metal Alloys with Monomers & Short-Chain Polymers 12
- Reactions of Coated Metal Alloys with Simulants DMMP & Thiodiethanol 14

RESULTS 17

- Experimental Matrices 17
- Polymerization Results via DSC 17
- Simulant Neutralization Results via LC 23

DISCUSSION 26

CONCLUSIONS 28

REFERENCES 30

- Patents 30
- Journals, Reports, Other 30

BIBLIOGRAPHY OF PUBLICATIONS 33

MEETING ABSTRACTS 33

LIST OF PERSONNEL 33

APPENDICES 34

APPENDIX A - EXPERIMENTAL MATRICES 35

APPENDIX B - ANOVA RESULTS OF EXPERIMENTAL MATRICES 39

APPENDIX C - DSC SCANS FOR REACTED METAL POWDERS 46

APPENDIX D - LC RAW DATA AND STATISTICS 93

This document contains CONFIDENTIAL and PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the expressed written permission of Mainstream.

INTRODUCTION

SUBJECT

The subject of this research and development effort is skin protectants which are effective barriers and neutralizing agents for chemical warfare (CW) agents. The neutralization or immobilization of CW agents such as sulfur mustard or nerve agents (GA, BG, BD, and VX) are of particular interest. Typically, the neutralizing agents are incorporated into a base cream, containing a mixture of perfluorinated polyether oil and Teflon particulates as thickener, for application to the skin as a protectant from cutaneous exposure to these agents. The complete product, base cream and neutralizing agent, must not be harmful to skin or be toxic by absorption.

The development of non-harmful, non-toxic, highly efficacious skin protectants for personnel routinely exposed to toxic materials (e.g., toxic chemicals, nerve agents, plant related toxins such as poison ivy, pesticides, and herbicides) would be in demand for both military and commercial applications. These protectants would be extremely useful for chemical warfare environments, police riot control, and campers where exposure to poisonous plants and animals are possible. Deathly allergic persons could also use these topical substances to prevent reaction.

PURPOSE

The ultimate purpose of this research effort was to develop neutralizing compounds, which when incorporated into a base cream, provide a barrier against CW agents and other toxins. The material should be affordable, safe and non-irritating, chemically stable, and demonstrate rapid kinetics. To achieve this ultimate objective, our Phase I research objectives were designed to (1) determine the feasibility of coating reactive metal powders with polymers, rendering them more easy to handle and inert to physical contact, and (2) evaluate the neutralizing potential of these coated powders toward CW agent simulants. The experiments developed to achieve these goals proved the feasibility of selected metals and polymer combinations and also helped us identify other metals and alloys which could be equally effective.

SCOPE

The scope of this effort was to research a "new" class of CW neutralizing compounds by screening a large number of activated metal alloy powders having an organic coating produced by reaction with monomers or shorter-chain polymers. To rapidly screen numerous combinations of the metals and polymers within the compressed time-scope of a Phase I effort, we chose two techniques: differential scanning calorimetry (DSC) to quantify the extend of metal/monomer reaction, and liquid chromatography (LC) to measure the neutralizing potential of 2 CW agent simulants. This research scope encompasses the technology areas of metal hydrides, catalysis, *in situ* polymerization with metals, and CW agent neutralization or immobilization. Per DoD SBIR Solicitation 96.2 Topic A96-143, efficacy testing will be

This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the expressed written permission of Mainstream.

conducted by the Army medical Research Institute for Chemical Defense. The tasks undertaken in this effort are listed below:

- *Task 1:* Develop the Definition of a Successful Protectant: Identification of CW simulants and definition of the protective agents.
- *Task 2:* Identify Several Metal Substrates and Monomers: Select candidate metal and/or metal oxides, and monomers for raw materials in producing the coated protective agents.
- *Task 3:* Design and Fabricate Laboratory Test Apparatus: Assemble the test and production apparatus for preparing the metal/metal oxide coated agents.
- *Task 4:* Perform Activation and Polymerization Experiments, and Evaluate Destruction Capability of Materials: Perform metal/metal oxide preparation and polymer coating experiments, and optimize process variables.
- *Task 5:* Demonstrate the Destructive Potential of the Coated Metals to Army Personnel: The most-feasible production process and neutralization or immobilization capabilities of the powders will demonstrated to the Army via live, video or graphical slide presentation at Mainstream Engineering.
- *Task 6:* Develop Preliminary Phase II Designs From Optimum Phase I System Components: Develop a first estimate scale-up design for the most-feasible powder production process.

The research carried out to accomplish these tasks is described below, broken down by Experimental Methods and Materials, Results, Discussion, and Conclusions.

BACKGROUND OF PREVIOUS WORK

There are two areas of previous research to discuss having relevance to this research effort: (1) metal oxide and hydride catalyzed reaction or polymerization, and, (2) chemical warfare (CW) agent destruction catalysts and protective chemicals. These specific technology areas are surveyed in the following section.

metal oxide and hydride catalyzed polymerization

Many metal and metal alloy oxides are used in catalysis, and metal hydrides are used in chemical synthesis as reducing agents or catalysts. The metal alloy substrate candidates selected for this effort are $TiFe_{0.9}Mn_{0.1}$, Mg_2Ni, and $CaNi_5$, each of these having the ability to form reversible metal hydrides. These alloys were selected because alkali metals have been used in the past in skin protectant formulations as a reactant for CW agents, and metal oxides such as TiO_2 and MgO are known to act as catalysts in polymerization reactions.

Altemore and Ort [1975], Ziegler et al. [1977] and Miro [1990] have demonstrated the utility of metal and organo-metallics as a catalyst for polymerization process, however, the integration of the metal or organo-metallic into the final product was not the focus. Prior art in the areas of encapsulation of metals and metal compounds was also found in our literature search. Murphy

and Lajoie [1996] describe a $NaHCO_3$ polymer coated particle for use in anti-perspirants, metal oxides and carbonates have been encapsulated by radiation-induced vapor phase polymerization at 25-65 C with vinyl monomers by Bruk and Kirpikov [1995], Ono and Takahashi [1989] illustrate the spontaneous polymerization of methyl methacrylate in the presence of Cu, Al or Ni powders, Matsumura and Nakabayashi [1988] also describe the coating of TiO_2 particles by aqueous phase polymerization of methyl methacrylate, and Yamaguchi et al. [1975] polymerized methyl methacrylate onto Al, Fe, Cu, or Ag surfaces in aqueous SO_2.

Although there have been no prior demonstration of vapor or liquid phase polymerization using activated metal as the sole polymerization initiator, we theorized in our Phase I proposal that the extreme activity of the activated metal surface, whether hydride or oxide, could provide a very chemically or catalytically active environment. For example, the presence of dissociated hydrogen at the surface of the metals could be an effective free-radical initiator for olefins such as ethylene, tetrafluoroethylene, propylene or perfluoropropylene. Methyl methacrylate also polymerizes by the mechanisms of free-radical propagation. As another example, the metals Li and Na have also been proven to be effective anionic polymerization catalysts, so it is feasible that other metals such as Mg, Ca, Ni, Ti, Fe, and Mn could promote polymerization. Cationic polymerization is also catalyzed by acids, so it is conceivable that the presence of dissociated hydrogen (H+) at the metal surface would be an effective catalyst.

CW agent destruction and protective chemicals

There have been many skin-protective formulations developed over the past 30 years to serve as barriers to CW agents such as sarin, soman, and mustard gas. Unfortunately, many of the chemicals which can decomposed these toxic CW's also react with or irritate the skin. Others have only been proven effective toward specific agents and many are barriers, not chemical neutralizing or immobilization agents.

Many of the skin protectants developed to date, whether for CW agents or as sunscreens, use alkali metals, hydroxides, or salts as the active ingredient. For instance, Dahms [1994] describes a sunscreen composition comprised of a dispersed metal oxide in oil, Bannard et al. [1991,1993] specify a chemical warfare decontamination composition containing an alkali earth metal salt, Hammond and Forster [1991] suggest the use of polymeric amine-copper complexes to catalytically hydrolyze Soman, and Steyermark [1974] uses a strong base mixture including an alkali hydroxide to neutralize chemical warfare agents. Klabunde et al. [1987,1990], Koper et al. [1993], Yong et al. [1991,1992], Gruber [1995], and Back et al. [1995] have documented the use of metal oxide powders in the destruction of hetero-atom organic compounds such as dimethyl methylphosphonate (DMMP) and halogenated solvents. Other compositions make use of transition metals to catalyze the destruction of the CW agent or toxin. For example, Leslie and Ward [1992] describe the effectiveness of oxone (potassium peroxymonosulfate) in the presence of Co, Cr or Mn for the oxidation of sulfur (S) contained in mustard gas.

Other topical protectants make use of polymers to neutralize or form a barrier to CW agents or toxins. For example, silicone (i.e., poly-dimethylsiloxane) copolymers have been used in skin-

This document contains CONFIDENTIAL and PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the expressed written permission of Mainstream.

protecting formulations [Sasaki, 1990], polymerized alkyl methacrylates have been proposed as skin protectants [Sasaki and Saitoh, 1990], poly(ethylene glycol) methyl ether has been used as a reactive skin protectant for G and VX agents [Sawyer et al., 1991], and partially etherfied poly(ethylene glycol) with Na has also been studied as CW protectants. It has also been documented that the alkali metal Na will react with PEG and PEG methyl ether to form salts [Bannard et al., 1991] which are effective against CW agents. We suspect that the effect of Ca and Mg will be similar to Na. Other barriers may include Teflon particulates in a perfluorinated ether as described in the DoD SBIR 96.2 solicitation, Topic A96-143.

Physical barriers by polymer garments is also another route for protection from CW agents. Literature shows a range of polymers used in conjunction with chemical warfare agents, primarily for protection from penetration or protection for instrumentation and sensors. Polymers and other protective coating used include PVC [Jablonska, 1971], synthetic rubber with activated carbon [Hart, 1972], and vinyl chloride-ethyl acrylate copolymers [Braude and Lard, 1969]. Pal and Guy [1993] present permeation measurements for a variety of elastomers and plastics with CW agents. Of these, Nylon, and polyethylene seem to present the least resistance to CW agent permeability, and Viton, Teflon, neoprene, and polyester usually show the highest resistance to penetration. For our application of coating metal powders, the most permeable polymer would be desirable since the CW agents must diffuse to and from the surface of the metal to be neutralized.

This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the expressed written permission of Mainstream.

EXPERIMENTAL METHODS AND MATERIALS

The experimental methods employed during this research effort involved (1) the hydride cycling and activation of the metal alloy materials, (2) reaction of the activated metal alloy materials with monomers and short-chain polymers yielding "coated metal alloys", and (3) the reaction of coated metal alloys with the simulants DMMP or TDE. The flow chart for our experimental evaluation is shown in Figure 1. Each of these experimental procedures and the analytical tools used to measure the results are described in subsequent sections.

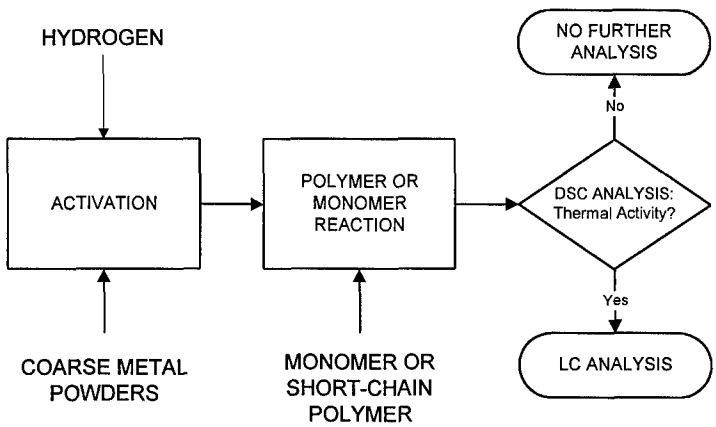


FIGURE 1 - Flow Chart For Experimental Procedure

METAL ALLOY PREPARATION AND ACTIVATION

The apparatus used to prepare the metal hydrides are shown in Figure 2. This system consists of three separate knife-edge flange 304 stainless steel reactors of about 60 ml in volume. Approximately 25-50 g of coarse alloy material is added to the reactors, sealed, and evacuated to 0.2 torr or less prior to introducing hydrogen. Hydrogen overpressure of 100-500 psia is typically used to activate the metal, the specific pressure being a function of the moles H_2 per mole metal which can be absorbed and the 1 L charging cylinder used. After the metal absorbs the hydrogen, the reactor is heated with a heater band and evacuated to desorb the hydrogen. This absorption-desorption process is then repeated a number of times to decrepitate the powder to finer and finer scale, creating and exposing more and more active surface area. The final result of this process is a very clean and active metal interface on a relatively high surface area powder. The surface area, depending on the number of absorption-desorption cycles, can range from about 0.1 to 10 m^2/g for particle sizes of 0.1-10 μm.

At the completion of the final desorption cycle, the alloy is either hydrided by a final exposure to hydrogen, or slowly exposed to air to produce a clean metal oxide layer on the powder. This final form, hydride or oxide, is then carried through to the next stage of the experiments: *reaction with a monomer or polymer.*

This document contains [redacted] and PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the expressed written permission of Mainstream.

selected metal alloys

The alloys chosen for study were Mg_2Ni, $TiFe_{0.9}Mn_{0.1}$, and $CaNi_5$. These alloys were selected so as to give us the broadest range of metal types (alkaline & transition) and a range of potential catalytic activity as suggested by prior literature. A broad range of hydride equilibrium pressures was also a factor in selection so that we were able to vary the residual hydrogen remaining in the material when it was reacted with the polymer or monomer. For example, Mg_2Ni will desorb hydrogen at a pressure of 14.7 psia at a temperature of about 250 C, whereas for the same H_2 pressure $CaNi_5$ must only be heated to about 40 C and $TiFe_{0.9}Mn_{0.1}$ to 0 C. Other candidates considered include TiFe, $LaNi_5$, Mg_2Cu, Mg_2Al_3, $Zr(Ni_{0.95}M_{0.05})$, $Ti(Fe_{0.8}Ni_{0.2})$, $ZrFe_{1.5}Cr_{0.5}$ and LiAl, where M is a mischmetal defined as a combination of Ce, La, Nd, Pr and other rare earth metals. The 3 alloys selected cover the ordinary reversible hydride pressure-temperature range (see Figure 3 described later).

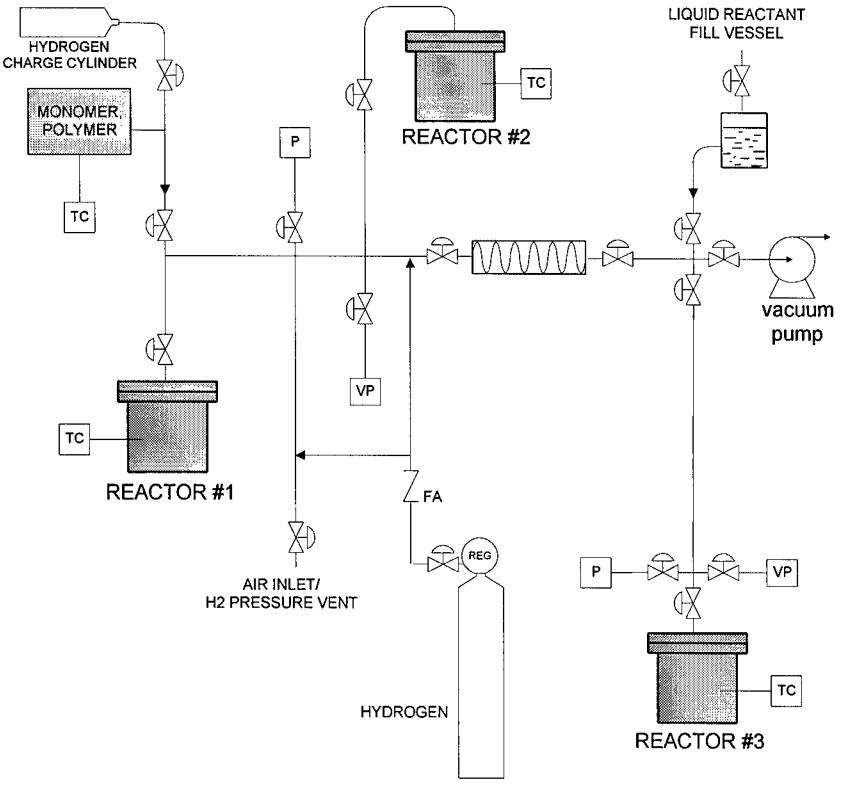


FIGURE 2 - Diagram of Activation and In Situ Polymerization Coating System
(TC=thermocouple; P=pressure gage; VP=vacuum pressure gage; FA=flash arrestor)

metal activation process

The activation process is carried out by cycling the metal alloy through successive absorption and desorption cycles with hydrogen. The metal alloys selected are generally used for applications of hydrogen storage or gettering. Thus, these materials reversibly absorb and desorb hydrogen. Below are the stoichiometric reactions of the alloys with hydrogen:

This document contains [redacted] and PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the expressed written permission of Mainstream.

$$TiFe_{0.9}Mn_{0.1} + H_2 \leftrightarrow TiFe_{0.9}Mn_{0.1}H_2 \quad [1]$$

$$Mg_2Ni + 2H_2 \leftrightarrow Mg_2NiH_4 \quad [2]$$

$$CaNi_5 + 3H_2 \leftrightarrow CaNi_5H_6 \quad [3]$$

It is important to note that the absorption (forward reaction) and desorption (backward reaction) do not directly involve the consumption and evolution of diatomic hydrogen gas, but rather, an intermediate step comprising dissociated hydrogen:

$$H_2 \leftrightarrow 2H^* \quad [4]$$

where H* is dissociated hydrogen present in the bulk and/or the surface of the metal substrate. Therefore, monatomic hydrogen can be available as reactant for polymerization or other reactions which is a key attribute of this research approach.

The reactions depicted by Equations 1-4 are temperature and pressure dependent and typically characterized by a van't Hoff plot. There is generally hysteresis of the absorption and desorption relations, however, Figure 3 summarizes the average equilibrium pressure with temperature relationship for the 3 alloys chosen in this Phase I research. The long-dash horizontal line in the figure is ambient pressure equal to 14.7 psia.

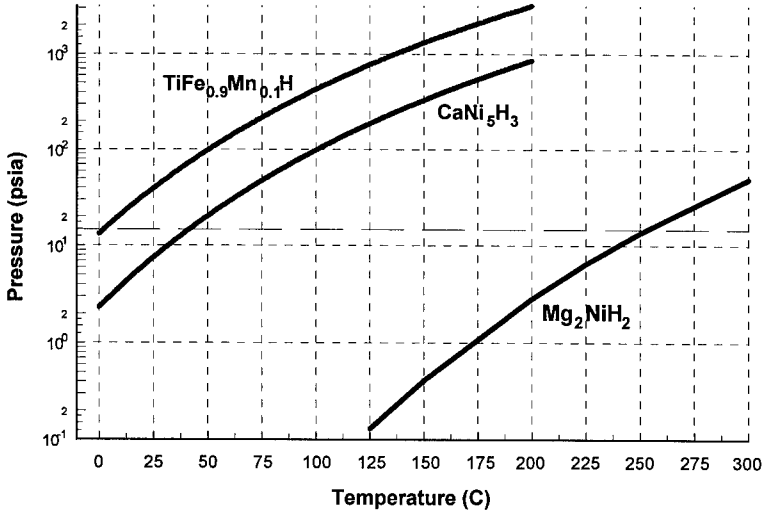


FIGURE 3 - Approximate Hydrogen Sorption Equilibrium Curves for 3 Metal Alloys
(mid-plateau stoichiometry and average of desorption and absorption pressures)

Prior to introducing monomers or polymers to the activated metal in the reactor, the metal is either hydrided or oxidized as a final step. To prepare a metal hydride for reaction with the

monomer or polymer, the metal is left in a state represented by the right hand side of equations 1-3. If we prepared an active oxide, the desorbed metal alloy is slowly exposed to air so as to allow the oxygen to react with the active metal and form an oxide. This reaction is illustrated by equation 5:

$$Me_n + \frac{x}{2}O_2 \leftrightarrow Me_nO_x \qquad [5]$$

where Me_n represents some generic metal alloy such as Mg_2Ni, $TiFe_{0.9}Mn_{0.1}$, and $CaNi_5$. This reaction is typically exothermic and irreversible. The oxide can, however, be removed by hydriding the metal (which is one purpose of the activation process) --- this forms H_2O on the metal surface which can be removed by vacuum and heat treatment.

REACTIONS OF ACTIVATED METAL ALLOYS WITH MONOMERS & SHORT-CHAIN POLYMERS

After preparing the metal powders by the hydride cycling activation process, the metals were then exposed to a variety of monomers or short-chain polymers in the same reactor used for hydriding as shown in Figure 2. The resulting materials are then opened to the ambient, removed from the reactor, sampled, and scanned by DSC for thermal activity.

TABLE 1 - PROPERTIES OF POLYMERS AND MONOMERS

COMPOUND	MW (approx.)	normal b.p. (C)	melting point (C)	state at 25 C
methyl methacrylate	100	103	-48	LIQ
perfluoropropylene	150	-29	-156	GAS
propylene glycol butyl ether	132	171	no data	LIQ
poly(methyl methacrylate)	996,000	decomp	274	SOL
poly(propylene)	12,000	decomp	161	SOL
poly(tetrafluoroethylene)	varies	decomp	327	SOL
poly(dimethylsiloxane)[a]	varies	decomp	no data	LIQ
silicone	varies	decomp	> 250	LIQ
poly(ethylene glycol)	300[b]	~375	> -10	LIQ
poly(ethylene glycol) methyl ether	350[c]	~378	> -8	LIQ
perfluoropolyether-X175/08	varies	160-215[d]	-45	LIQ

a) precursor for silicone rubbers, broad range of molecular weights
b) poly(ethylene glycol) solid at room temperature when MW exceeds about 600
c) poly(ethylene glycol) methyl ether solid at room temperature when MW exceeds about 550
d) boiling range at 0.05 mm Hg vacuum

selected monomers and short-chain polymers

The monomers and polymers selected for our experiments are a cross-section of olefin-derived, glycol, glycol-ether compounds, acrylic, and inorganic siloxanes. The polymers include polypropylene, polyethylene, Nylon, poly(methyl methacrylate), poly(ethylene glycol) or PEG,

poly(ethylene glycol) methyl ether, and poly(dimethylsiloxane); the monomers used in our experiments were hexafluoropropylene, methyl methacrylate, and propylene glycol butyl ether. These polymers and monomers were chosen in light of our literature search of metal and metal oxide catalyzed polymerization reactions and the most successful monomers used by other researchers. Some of the short chain polymers were also chosen because they are sometimes used in protectant skin cream formulations either as an active ingredient or as a base. Another factor in our selection was toxicity.

This group of compounds gave us a range of polymer and monomer types (olefins, poly ethers, poly glycols, methacrylates), fluid states (gas, liquid), and physical properties (melting points, boiling points, chemical resistance). A summary of these compounds and some of their physical properties is given in Table 1.

DSC measurements

To determine the extent to which the metal substrate has catalyzed the formation of organic fragments on the metal, we employed differential scanning calorimetry (DSC). This method detects thermal "events" such as polymer glass transition, melting endotherms of solids, boiling endotherms of liquids, fluid heat capacity, oxidation stability, purity, or heat of reaction. The DSC instrument used in our lab is a Mettler DSC 27HP with a Mettler TC11 TA processor running Mettler GraphWare TA72. This instrument can detect minute heat flow variations (~0.025 mW) and is accurate to within about 0.5 C.

After completion of the polymerization process, an aliquot of the 25-50 g metal alloy sample is removed from the reactor and placed in a 40 μL DSC sample pan. Sample sizes ranged from about 10-100 mg. The sample was then purged with nitrogen at 0.5-1.0 L/min and scanned in temperature from about 30 C to the first appearance of an endotherm or exotherm. After the first endotherm or exotherm has resumed back to a base line the scan is stopped and the sample is allowed to cool back to below this endotherm or exotherm temperature. We then restart the DSC scan to check for the re-appearance of the endotherm of exotherm and continue up through the next endotherm or exotherm. This procedure was repeated until no further endotherms or exotherms were detected or a temperature of 450 C was reached. The reason for this step-wise protocol was to gain more information about the source of the endotherm or exotherm.

For example, an endotherm for a methyl methacrylate reacted powder at approximately 100 C probably indicates the boiling of methyl methacrylate, and a re-scan should show that this peak disappeared since it will have boiled off. If a peak is still present in the re-scan, then it is probable that the endotherm was caused by polymer melting and re-melting indicating that the metal substrate has polymerized the monomer. In many cases we also detected endotherms or exotherms which appear in the first scan, then upon re-scanning this peak disappears and another appears. As another example, we observed n predominant exotherm for many Mg_2Ni powders at approximately the temperature at which the hydrogen desorption pressure would be 14.7 psia (approx. 250 C). Upon re-scan, a small endothermic peak appeared at about the same temperature, which we believe to be the endothermic hydrogen desorption reaction, followed by

This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the expressed written permission of Mainstream.

a large endothermic peak. One interpretation of this event is that the desorbing hydrogen in the presence of the monomer fluid caused an endothermic reaction, presumably polymerization, which produced a product having a melting and/or boiling point seen by the newly formed peak.

REACTIONS OF COATED METAL ALLOYS WITH SIMULANTS DMMP & THIODIETHANOL

Many of the coated metals which showed thermal activity using the DSC (indicating the presence of monomer or polymer) were subjected to testing with the CW simulants DMMP and TDE. The method used was a custom LC technique developed specifically to ascertain whether or not the coated metal produced a statistically significant neutralization or immobilization of the simulant. This involved an F-test between 2 pools of data: one pool for a baseline or "as-received" powder substrate, and another pool for a polymer-reacted powder from the experiments. This experimental protocol was developed to determine whether or not there was a significant neutralization or immobilization of the simulant and the approximate % neutralization or immobilization.

chemical warfare agent simulants

We selected two simulants for testing the neutralizing potential of the coated metal powders. This selection was based on a literature survey of simulants used in past research efforts and similarities in chemical structure and properties [Reifenrath et al., 1984; Copa and Momont, 1995; Berg et al., 1995; Blank, 1993; Davis et al., 1992; Berg et al., 1995; Cataldo et al., 1988; Pal et al., 1993]. These properties include individual atoms (e.g., S, P, O), molecular fragments (e.g., -O-P=O, $-CH_2-S-CH_2-$, solubilities, polarity or electronegativity at the heteroatom, and fluid state at room temperature. Figure 4 shows a molecular comparison of nerve agents and mustard gas to a host of simulants suggested or used in previous research studies. We chose DMMP and TDE based on their favorable chemical structure similarities to their CW counterpart, low toxicity relative to the other simulants, and the arguments of Blank [1992] who also selected these agents for supercritical water oxidation studies and their similarities in chemical and physical properties to CW agents.

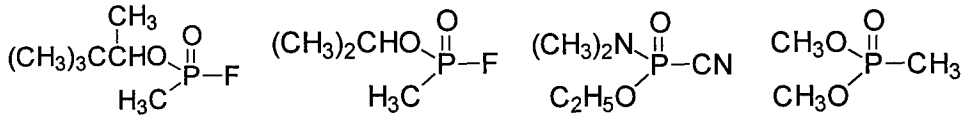


FIGURE 4 - Simulants and CW Agent Analogs

liquid chromatography method

We developed a custom LC method to screen for efficacy of the coated powders produced by the monomer or short-chain polymer reaction with the metal alloys. The equipment used for these measurements were an *Alltech* HPLC with UV/VIS detector and a *Chromjet* SP4400 integrator.

The basis of the method rests on several assumptions and they are as follows:

1) The load of DMMP and thiodiethanol on the metal will not exceed five percent of the total weight,
2) the reaction time is quick, less than 15 minutes,
3) the compounds are fully extractable by acetonitrile or water from the metallic surface,
4) that there are no reactions between DMMP and thiodiethanol and acetonitrile or water, and
5) both DMMP and thiodiethanol can be analyzed reliably using HPLC.

A sample is processed by first obtaining a known amount of metal sample (usually about 2.0 - 2.5 grams) and putting it into a 10 mL volumetric cleaned dry flask. Then, two to three drops of DMMP or thiodiethanol (a mass of 0.02 to 0.06 grams) is added and weighed to the nearest 0.0001 gram. This will bring the percent DMMP or thiodiethanol relative to the total weight to between **1 and 5 percent**. The DMMP or thiodiethanol is shaken with the metal solid to insure complete mixing and left to stand for 15 minutes, after which acetonitrile or water is added to the 10 mL mark on the volumetric flask. The acetonitrile or water is then filtered with a 0.45 mm filter, injected into the HPLC and analyzed for concentration of either DMMP or thiodiethanol. The concentrations are calculated as grams of sample per injection loop (20 mL). To obtain percent concentration of either simulant, the area of the peak representing either simulant is used as a factor in a calibration equation yielding grams of sample per injection loop. The formula for calculating the percent concentration is shown below:

$$\%\ \text{simulant} = \frac{(\text{grams injected}) \cdot (10\ \text{ml extraction vol.})}{(0.02\ \text{ml injection vol}) \cdot (\text{sample weight, grams})} \qquad [6]$$

Conditions were optimized for both DMMP and TDE on the HPLC. For DMMP, a mobile phase of 20% acetonitrile and water was passed through a PRP-1 Hamilton column at a rate of 1.0 mL per minute. Peaks were found using a UV/VIS detector set at 200 nm with a retention time of approximately 1 minute. For thiodiethanol, a mobile phase of deionized water was passed through a PRP - X400 column at a rate of 1.5 mL per minute. Peaks were found using a UV/VIS detector set at 225 nm with a retention time of approximately 5.5 minutes.

Final results were calculated as a percent recovery of measured simulant quantity using HPLC and the above equation divided by the percent simulant actually mixed with the metal.

Accordingly, fifteen to 20 measurements per sample was selected to develop the statistical comparisons between the "raw powder" and the polymer-reacted powders. Twenty analyses per sample was deemed a reasonable number based on the desired level of confidence (95%) and inherent variability. The 15-20 sample size requirement for these tests (the minimum size for producing statistically significant results) directly follows published statistical procedures [Revelle, 1990]. Since there is considerable variation of HPLC results for the DMMP analysis, many repeats were necessary to certify statistical differences of the polymer-reacted samples relative to the raw, un-activated powder.

Statistical comparisons were done using Analysis of Variance (ANOVA), a method that compares the sums of squares (square of difference between samples and the mean) within a group and its mean to the sums of squares (square of difference between samples and the grand mean of all samples) between groups. The ratio of these two numbers is also known as the F value, and the test is the F-test. If the difference between groups is significantly greater than the difference within a group (large value for F) and the value is greater than the critical F-value (F_{crit}) published in statistics table, then the two data groups are different with a specific probability. The "groups" we are referring to here are (1) the LC data group generated for the raw powder, and (2) the LC data group of the polymer-reacted powder of the specific experiment.

This document contains [redacted]PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the expressed written permission of Mainstream.

RESULTS

EXPERIMENTAL MATRICES

The experimental matrices used to evaluate the polymerization experiments and CW simulant neutralization or immobilization are shown in Appendix A. The "thermal activity" and "peak count" of a particular combination of reaction temperature, monomer specie, monomer pressure, and metal alloy was graded on the semi-quantitative scale. The thermal activity takes into account the height of the thermal peak (an indicator of the amount of polymer or organic compound present), and the temperature range in which the peak appears. The peak count is not biased by the size of the peak which can be affected by the weight of the sample used. Both of these parameters correlate to roughly the same experiments as having the greatest DSC activity, and we therefore conclude that for our semi-quantitative assessment either parameter will be representative.

With regard to the feasibility grading, we analyzed each DSC scan and assigned values to the importance of peaks in 3 different temperature ranges. The first temperature range, 50-110 C, is deemed insignificant since the thermal activity in this region is most likely a result of boiling water residue or boiling monomer. The second "region" of thermal activity was assigned to 110-250 C. This temperature range would host thermal activity associated with most polymer melts and higher molecular weight organic compounds boiling. The highest temperature range, 250-450 C, would encompasses the melting of some polymers such as those derived from perfluorinated olefins (e.g., Teflon) , the boiling of large molecular weight organics. The entire range from 110-450 C would also show any exotherms associated with polymerization, and outside the temperature of about 400 C or possibly lower most organics will decompose or pyrolyze.

Using this rating system, we use statistical evaluation of the experimental matrices using Taguchi methods to determine the variables which have the greatest influence on the "response", which in this case is the feasibility parameters. Overall, the most influential "factors" in producing an active thermal scan ("response"), hence, the production of polymers or longer chain monomers from the monomers or short-chain polymers was ***the monomer or polymer reactant and whether or not the materials was kept in a hydrided state for the reaction.*** The hydride effect was hypothesized prior to the experiments since monatomic H (in the form of H^+ or free-radical H) will be present near or at the surface of the metal during desorption and absorption, and available as a possible source to fuel polymerization or reduction reactions.

POLYMERIZATION RESULTS VIA DSC

The Taguchi orthogonal array experimental results for the experiments in Appendix A are summarized in Appendix B. DSC scans measured for the experiments of Appendix A are shown in Appendix C. Table 2 also summarizes the data by experiment. Below is a summary and discussion of the results for each experimental set.

This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the expressed written permission of Mainstream.

TABLE 2 - DSC Thermal Activity Results[a]

	Endotherms-T(C)			*Exotherms-T(C)*			*DSC peaks:*	
EXP'T	**50-110**	**110-250**	**250-450**	**50-110**	**110-250**	**250-450**	**peak count[b]**	**thermal activity[b]**
CaNi-1	1S						0	0
CaNi-2	1L						0	0
CaNi-3	-	-	-	-	-	-	0	0
CaNi-4	-	-	-	-	-	-	0	0
CaNi-5	1M					1S	1	1
CaNi-6	1M					1S	1	1
CaNi-7	1M					1S	1	1
CaNi-8	1L						0	0
TiFeMn-1	1M						0	0
TiFeMn-2	1S						0	0
TiFeMn-3	-	-	-	-	-	-	0	0
TiFeMn-4	-	-	-	-	-	-	0	0
TiFeMn-5	1M	1L				1S	2	11
TiFeMn-6	1M	1L				1S	2	11
TiFeMn-7	-	-	-	-	-	-	0	0
TiFeMn-8		1S					1	1
MgNi-1	1M						0	0
MgNi-2	1S						0	0
MgNi-3			1M,1L				2	15
MgNi-4		1M	1L				2	15
MgNi-5	1L	2S,1M	1M,1L				5	22
MgNi-6	1M	2S,1M	1L				4	17
MgNi-7		2S,1M	1L				4	17
MgNi-8		1S	1M,1L				3	16
DLC-1		1S					1	1
DLC-2	1S	1S	1S,1M				3	8
DLC-3	1S						1	0
DLC-4		3S			1S	1S	5	5
DLC-5			1S				1	1
DLC-6		3S			1M		4	8
DLC-7		1S	1S		1M	1L	4	17
DLC-8	1S	1S	1S,2M		1M		5	17

a) thermal activity parameter based on scale: S=1, M=5, L=10 .... excludes the 50-110 C column; peak count is equal to the number of peaks, regardless of size, excluding 50-110 C
b) Legend: S=small peak (0-5 mW); M=medium peak (5-25 mW); L=large peak (>20 mW)

$CaNi_5$ Oxide Substrates (CaNi-1 through CaNi-4): The conditions and experimental array for this series is shown in Table A-1 (Appendix A), experimental results are summarized in Appendix B, and the raw data DSC scans are given in Appendix C. Referring to the scans for experiments CaNi-1 through CaNi-4, we see a primary endotherm at about 10 C +/- 10 C for the methyl methacrylate runs, and no discernible peaks for the perfluoropropylene runs. Re-scans do not show any reoccurring peaks. We conclude from this that little, if any, monomer has been polymerized by these substrates. Note that the normal boiling point of methyl methacrylate is

~100 C. The Taguchi ANOVA analysis of the results is given in Appendix B. This evaluation will identify the significant variables or "factors" which contribute most significantly to the "response," which in this case is the DSC "thermal activity" parameter described in Table 2. For this group of experiments, no significant differences in responses were observed.

$CaNi_5$ Hydride Substrates (CaNi-5 through CaNi-8): The conditions and experimental array for this series is shown in Table A-2 (Appendix A), experimental results are summarized in Appendix B, and the raw data DSC scans are given in Appendix C. These experiments produced a metal substrate comprised of a metal hydride of the alloy. Consequently, hydrogen (both monatomic and diatomic) will be present as a reactant at the surface of the metal and in the vapor space. Both experiments CaNi-7 and CaNi-8 show an endotherm at 74-83 C. Since the melting and boiling point of perfluoropropylene are -156 C and -29 C, respectively, this peak is can not be associated with the monomer. This endotherm, whether melting or boiling, suggests the presence of a longer chain organic which must be a polymerization or reaction product of perfluoropropylene. We surmise that the polymerized product of this monomer would have characteristics related to PTFE or tetrafluoropolyethylene $[-CF_2CF_2-]_n$, polypropylene $[-CH_2CH(CH_3)-]_n$, and polyvinyl fluoride $[-CH_2CF_2-]_n$ since hydrogen may be present in the metal substrate bulk to act as free radical. Experiment CaNi-7 also shows an ***exothermic*** peak at about 343 C. The origin of this peak is unclear, but it may represent the exothermic decomposition of the compound associated with the lower temperature endotherm. Experiments CaNi-7 and CaNi-8 were reported on in Monthly Technical Report #4 [Back, 1996-97]. The powder of Experiment CaNi-8 has also been tested in neutralization studies with DMMP and 2,2'-thiodiethanol. Both CaNi-5 and CaNi-6 powders show an endotherm at low temperatures (75-100 C), probably associated with the boiling of moisture or methyl methacrylate (b.p. = 103 C), followed by an exotherm at elevated temperatures (~370 C). This exotherm is interpreted as a reaction, either polymerization of decomposition of an organic substance present on the powder. In either case, the presence of an exotherm suggests that an organic phase/compounds is probably present.

The Taguchi ANOVA analysis of the results are also given in Appendix B. For this experimental set, there was no predominantly significant "factor" producing the DSC "thermal activity" variable defined in Table 2.

Mg_2Ni Oxide Substrates (MgNi-1 through MgNi-4): The conditions and experimental array for this series is shown in Table A-5 (Appendix A), experimental results are summarized in Appendix B, and the raw data DSC scans are given in Appendix C. Referring to experiments MgNi-1 through MgNi-4 we see the appearance of the ~100 C endotherm for the methyl methacrylate experiments. For the perfluoropropylene experiments (MgNi-3 & MgNi-4) two endotherms at higher temperatures are found. The first endotherm is at approx. 246-262 C and the second endotherm is at 355-368 C. We surmise that the polymerized product of this monomer would have characteristics related to PTFE or tetrafluoropolyethylene $[-CF_2CF_2-]_n$, since the monomer for both polymers is a perfluoro-olefin. Since PTFE ("Teflon") has a very high melting point (327 C) relative to other polymers, we suspect that polymerized perfluoropropylene would behave similarly. Therefore, the lower temperature endotherm present in MgNi-3 and MgNi-4 could be associated with polymer melting (which suggests that

polymerization did occur) and the higher temperature endotherm is the boiling of the liquid polymer. However, when the materials shown in the DSC scans were re-scanned up through the first endotherm, cooled, and continued scanning to 450 C the second endotherm was still present. This suggests that the two peaks are ***unrelated***. Another interpretation is that the first endotherm is residual hydrogen desorption when the hydrogen equilibrium pressure is approximately 1 atm. The second endotherm may be product formed from the reaction of this desorbing hydrogen with the monomer/polymer present around the particles. The Taguchi ANOVA analysis of the results is given in Appendix B. The analysis identifies the monomer perfluoropropene as the most significant contributor to producing a thermal activity. We translate this to mean that perfluoropropene has the greatest polymerization potential with Mg_2Ni. The effects of varying temperature and monomer pressure were insignificant relative to the polymer type.

Mg_2Ni Hydride Substrates (MgNi-5 through MgNi-8): The conditions and experimental array for this series is shown in Table A-6 (Appendix A), experimental results are summarized in Appendix B, and the raw data DSC scans are given in Appendix C. This hydrided substrate has produced the most interesting thermal behavior of all the materials. In experiment MgNi-5, we observed what is probably a boiling endotherm for methyl methacrylate at about 102 C, followed by a series of endotherms at elevated temperature (230-260 C), and a rather large endotherm at 407 C. We believe that the endotherms at about 238 C, which appear in Crv3, Crv4, and Crv5 for MgNi-5 in Appendix B, are associated with hydrogen desorption. The origin of the peak at 407.5 C is speculative, but may be a result of long-chain organic boiling or melting. This peak does not seem to be associated with the metal or metal hydride, so we presume it has organic origin. Experiment MgNi-6 is very similar to CaNi-5 with a series of peaks at around 240 C, and anther at 404.6 C. The interpretation is similar. Experiments MgNi-7 and -8 used perfluoropropene as the reactant monomer. The peaks at around 240 C appear also for these experiments, however, a peak at 335 and 356 appear rather than at 404-408 C. This confirms that the monomer-related products formed from the methyl methacrylate and perfluoropropene reaction are different (as they should be). The size of the peaks at 335 and 356 C also demonstrate that a large amount of the compound is present.

The Taguchi ANOVA analysis of the results are also given in Appendix B. For this experimental set, there was no predominantly significant "factor" producing the DSC "thermal activity" variable defined in Table 2. The analysis identifies a similar contribution to the DSC thermal activity by all three variables, reaction T, monomer pressure, and monomer type. We conclude that all are important for this Mg_2Ni hydride. It may be more significant that the alloy is hydrided which masks any effect of the other variables. This seems to be supported by the relative difference in DSC feasibility numbers between the Mg_2Ni oxide and Mg_2Ni hydride experiments.

$TiFe_{0.9}Mn_{0.1}$ Oxide Substrates (TiFeMn-1 through TiFeMn-4): The conditions and experimental array for this series is shown in Table A-3 (Appendix A), experimental results are summarized in Appendix B, and the raw data DSC scans are given in Appendix C. Referring to the scans for experiments TiFeMn-1 through TiFeMn-4, we see a primary endotherm at about 10 C +/- 10 C for the methyl methacrylate runs, and no discernible peaks for the perfluoropropylene

runs. Re-scans do not show any reoccurring peaks. We conclude from this that little, if any, monomer has been polymerized by these substrates. The Taguchi ANOVA analysis of the results is given in Appendix B. For this group of experiments, no significant differences in responses were observed.

$TiFe_{0.9}Mn_{0.1}$ Hydride Substrates (TiFeMn-5 through TiFeMn-8): The conditions and experimental array for this series is shown in Table A-4 (Appendix A), experimental results are summarized in Appendix B, and the raw data DSC scans are given in Appendix C. The experiments involving methyl methacrylate (TiFeMn-5 and TiFeMn-6) showed similar behavior: an endotherm at approximately 103.5 C, assumed to be the boiling of methyl methacrylate, followed by another endotherm at 143 or 135 C. This second endotherm is interpreted as a melting or boiling endotherm of another organic compound. The sharpness of the peak also indicates a relatively pure phase (i.e., not a broad melting or boiling as would be expected with a range of molecular weight compounds). There also appears to be a slight exotherm for these two experiments at higher temperatures (~ 350 C). None of these peaks should be associated with metal hydride desorption since the hydrogen desorption pressure at temperatures greater than 25 C exceed 40 psia. Consequently, the chemical potential of the hydrogen present the metal lattice will be very large even at room temperature, and the metal should easily desorb before the temperature of 140 C is reached (equilibrium hydrogen pressure at 140 C is greater than 1000 psia). Experiments TiFeMn-7 and -8 with perfluoropropene show little or no thermal activity, except for a slight endotherm for TiFeMn-8 at ~ 156 C.

The Taguchi ANOVA analysis of the results is given in Appendix B. The analysis identifies the monomer methyl methacrylate as the most significant contributor to producing thermal activity. We translate this to mean that methyl methacrylate has the greatest polymerization potential with $TiFe_{0.9}Mn_{0.1}$. The effects of varying temperature and monomer pressure were less significant relative to the polymer type.

Direct Powder/Liquid Contacting (DLC-1 through DLC-8): The conditions and experimental array for this series is shown in Table A-7 (Appendix A), experimental results are summarized in Appendix B, and the raw data DSC scans are given in Appendix C. These experiments first produced a metal substrate comprised of a metal hydride of the alloy, followed by exposure to a variety of monomers and short-chain polymers which are liquids at room temperature. At the completion of the reaction between the fluids and the metal alloy substrates, the reactor is opened and any excess fluid is drained off. Note that because of this preparation technique, hydrogen, both monatomic and diatomic, will be present as a reactant at and/or near the metal surface.

The DSC scans of DLC-1 show negligible thermal activity. The material used in experiment DLC-1 was poly(dimethylsiloxane). Since the polymerization of this category of polymers (silicones) usually involves water as a reactant [Ulrich, 1993], the additional experiments using this materials will include 5% water by weight before introducing to the activated metal substrate.

Referring to DLC-2, the product of Mg_2NiH_2 with poly(ethylene glycol) and 5% water shows several endotherm peaks (water is added as a potential initiator in the polymerization reaction). The first peak appearing at about 242 C could be related to hydrogen desorption. The peak at 291 C is interpreted as a reaction, and the peak at 394 is probably the boiling endotherm for poly(ethylene glycol) measured by DSC to be about 375 C. Experiment DLC-3 used a low-molecular weight silicone polymer, poly(dimethylsiloxane) with 5% water as polymerization initiator. The scan shows little or no thermal activity.

DLC-4 shows several exothermic and endothermic peaks. The first exothermic peak of scan "Crv 2" shows an exotherm at about 210 C, and successive scans show endotherms at about 240 C which we will contribute to hydrogen desorption. A high temperature exotherm at 377 C is also found for this material. The two exothermic peaks for DLC-4 are related to reactions between the metal and the short-chain polymers: One interpretation is that the exotherm at 209 C is the formation of a longer-chain compound which is later exothermically decomposed at 377 C. Experiment DLC-5 is a scan of the product of $TiFe_{0.9}Mn_{0.1}O_x$ and poly(ethylene glycol) and water. Little if any thermal activity is observed.

The product from experiment DLC-6 shows a very strong exothermic peak at about 213 C along with a series of endothermic peaks around 238 C. Again, we interpret the exothermic peak as the formation of compounds from the polymer reactant, and, the peaks at about 238 C as hydrogen desorption.

Experiment DLC-7 resulted in several exothermic and endothermic peaks. Exotherms appear at about 233 C and 333 C. Based on the hydrogen equilibrium behavior of the Mg_2Ni alloy, we deduce that the 233 C exotherm is ***related*** to hydrogen desorption from the metal. Since the desorption process itself is endothermic, this peak could be an exothermic reaction with the desorbing hydrogen masking the desorption endotherm. The re-scan supports this theory since an endotherm does appear at approximately 240 C, near the 1 atm hydrogen desorption pressure expected for the hydride material. The endotherm at 333 C is more difficult to interpret, especially since an endotherm appears upon re-scan at approximately the same temperature. The exotherm may represent a reaction of polymerization, and the endotherm on the re-scan could be a melting or boiling of this product.

Finally, experiment DLC-8 shows a strong exothermic peak at about 174 C. This is interesting because the boiling point (which would be an endotherm) is at about the same temperature (171 C). Therefore, the vaporization of the propylene glycol butyl ether seems to initiate some type of reaction, presumably with the metal substrate. A broad endothermic peak is also measured at around 286 C, which could be the boiling or melting of a product formed at the lower temperature.

We also compared the effect of powder scale on the DSC "thermal activity". Experiments CaNi-8, TiFeMn-5, and DLC-8 were repeated with a finer scale starting material. The DSC scans for these powders were similar to the scans for the larger scale starting material. These particular

This document contains [redacted]PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the expressed written permission of Mainstream.

samples were also submitted to the U.S. Army Medical Institute for Chemical Defense for independent testing with barrier cream formulations.

Finer Powders Sent to U.S. Army Medical Research ICD for Barrier Cream Tests: 3 sets of powders were prepared and sent to the U.S. Army Medical Research Institute for Chemical Defense for independent testing in barrier cream formulations. As of June 11, 1997, the results for these tests are still pending. DSC scans were performed on these powders to verify that the reaction process and products formed were similar to those observed for the coarser powders produced in the earlier experiments. As shown in Appendix C, these scans are similar to their coarser powder analogs: CaNi-8 (fine) compared to CaNi-8, DLC-8 (fine) compared to DLC-8, and TiFeMn-5 (fine) compared to TiFeMn-5. The fine powders which were not reacted with the monomer or polymer were also scanned revealing little or no DSC peaks in contrast to the same powders reacted with a monomer or polymer. From this we conclude that the peaks are not directly related to hydrogen desorption or other compounds in the raw material, and that the compound(s) producing the endotherms and exotherms are something other than the reactants. Due to time restraints, these materials were not analyzed via HPLC to compare their neutralization/immobilization capability toward TDE and DMMP with the equivalent coarser powders produced in earlier experiments. We assume that the similarities of DSC thermal activity will correlate to similar neutralization potential.

SIMULANT NEUTRALIZATION RESULTS VIA LC

The LC raw data and statistical analysis for selected experiments of Appendix A with relatively large values of thermal activity and peak counts are shown in Appendix D. Table 3 also summarizes the results by experiment where F is a measure of significant difference between the raw material and the monomer/polymer reacted material. F_{crit} is a cutoff defined statistically for a particular degree of confidence and number of data points in the data set. Any value of F larger than F_{crit} indicates that the difference between the two data sets is significant. Of the material combinations summarized in Table 3, the $TiFe_{0.9}Mn_{0.1}H$ + methyl methacrylate shows the highest overall immobilization percentage and also the highest F values. The Mg_2NiH_2 and perfluoropropene combinations were the least effective and least significant. The $CaNi_5H_3$ + perfluoropropene and the Mg_2NiH_2 + PGBE combinations showed a fairly significant immobilization of the DMMP but was ineffective toward the TDE.

Experiments were also performed to check the independent effect of the monomer on the immobilization or neutralization of TDE and DMMP. We measured no significant reduction in DMMP or TDE when exposing the simulants to methyl methacrylate and propylene glycol butyl ether mixed with an "inert" solid substrate of molecular sieves. We conclude that the reduction in DMMP and TDE measure via HPLC is a result of the metals substrate activity and/or organic products produced from the reaction of the metal substrate with the monomer or polymer.

Figure 5 is an illustration of the HPLC scans used to generate the results of Table 3. The full set of scans for all of the experiments and repetitions are not included in this Final Report due to the

volume, however, this data is located in the Chemical System Division's analytical lab filed by date, and is available upon request by the Army.

TABLE 3 - Summary of HPLC Neutralization/Immobilization Experiments

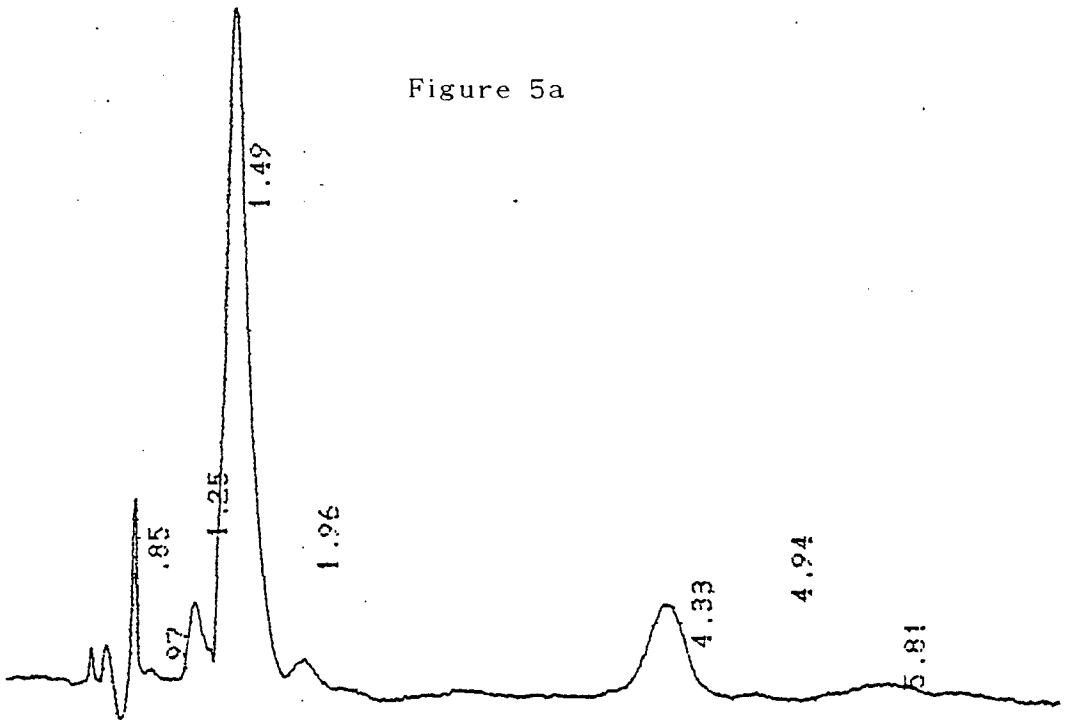
EXP'T	MATERIALS	No. data pts.	F_{crit}	F	immobilization or neutralization* (%)
TiFeMn-5	$TiFe_{0.9}Mn_{0.1}H$ + methyl methacrylate	15	4.2	343	22 (TDE)
TiFeMn-5	$TiFe_{0.9}Mn_{0.1}$ + methyl methacrylate	20	4.1	258	97 (DMMP)
MgNi-8	Mg_2NiH_2 + perfluoropropene	15	4.2	0.1	0 (TDE)
MgNi-8	Mg_2NiH_2 + perfluoropropene	20	4.1	1.1	0 (DMMP)
CaNi-8	$CaNi_5H_3$ + perfluoropropene	20	4.1	0.9	2 (TDE)
CaNi-8	$CaNi_5H_3$ + perfluoropropene	20	4.1	33	66 (DMMP)
MgNi-5	Mg_2NiH_2 + methyl methacrylate	15	4.2	1.2	3 (TDE)
MgNi-3	Mg_2NiO_x + perfluoropropene	15	4.2	12	0 (DMMP)
MgNi-3	Mg_2NiO_x + perfluoropropene	15	4.2	0.19	0 (TDE)
DLC-8	Mg_2NiH_2 + propylene glycol butyl ether	20	4.1	18	45 (DMMP)
* relative to the raw material (not treated with hydride cycling or exposed to monomers or polymers)					

Figure 5 illustrates a comparison of HPLC scans for experiment CaNi-8 and $CaNi_5$ raw material. The peaks confirmed to be DMMP via spike addition are located at retention times between 0.8 and 0.85 minutes. Note that there are negative and positive peaks in this range. We used both the negative and positive peaks for determining the DMMP neutralized or immobilized, both yielding approximately the same results. The presence of the two peaks is most likely a chromatographic effect associated with enriched acetonitrile and enriched DMMP zones within the "plug" of DMMP which emerges from the column. Most notably, there is a significant reduction in the peaks at 0.8-0.85 minutes between the two scans, especially when considering the fact that the CaNi-8 materials was exposed to about 2 times as much DMMP compared to the raw material.

The larger peaks at 1.5 minutes and 4.3 minutes are associated with organic impurities of the metal alloy or eluent. This is evident from the scans of Figure 5 since the concentration of DMMP used is double for the case of the CaNi-8 material (Fig. 5b) with no apparent change in peak height. If these peaks were by-products, one would expect them to change in proportion to the amount of DMMP used.

The peak at around 2 minutes and the shoulder at about 0.96-0.97 minutes is probably associated with DMMP impurities since their size increase when using more DMMP. Since these peaks are present even with the raw material (i.e., no hydride treatment or polymer/monomer coating), they are probably not associated with by-products or organics produced by the metal + perfluoropropene reaction.

This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the expressed written permission of Mainstream.



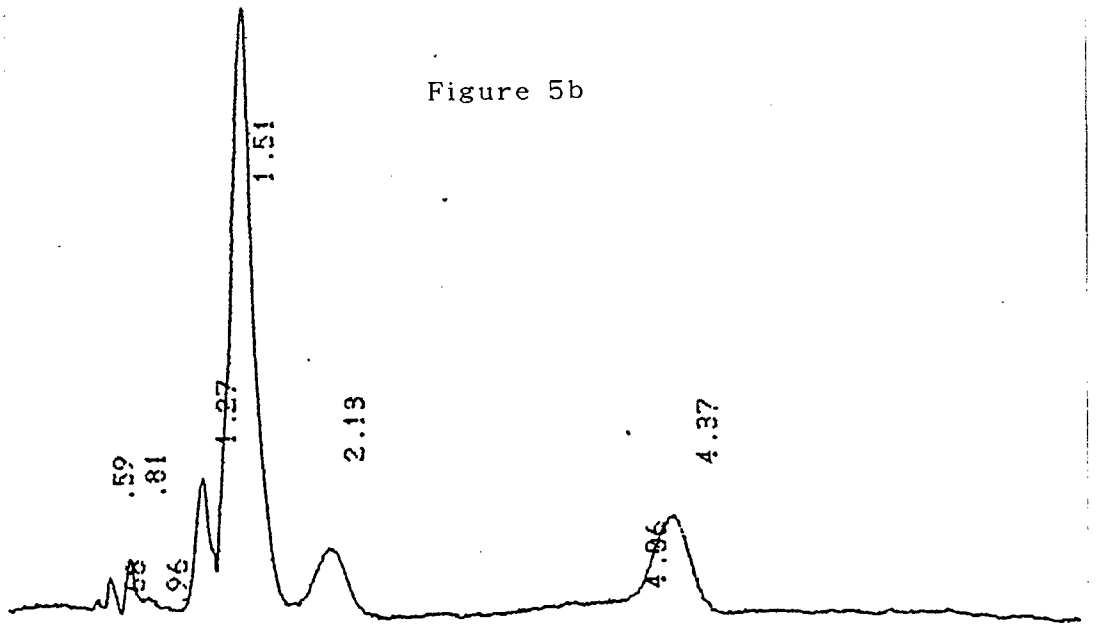


FIGURE 5 - HPLC Scans Comparison: (a) 1.75% DMMP with raw material $CaNi_5$, (b) 3.51% DMMP with powder of Experiment CaNi-8

This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the expressed written permission of Mainstream.

DISCUSSION

We break this discussion down into the polymerization process and the simulant neutralization or immobilization potential of the powders. As show on the RESULTS section, several powders produced endotherms and exotherms above the temperature range of ~110 C. Since nearly all polymers melt at temperatures above this, and there is a potential for water residue on the metal powder with a boiling point of 100 C, thermal "events" at or below this level are deemed insignificant. The polymerization experiments in summary produced about 20 combinations of metal alloys and monomer or short-chain polymers. The product of these "reactions" produced measurable endotherms or exotherms using DSC which we interpret to be related to the formation of polymers fragments or other products generated by the contact with the metal alloy powders.

Although there are much more rigorous methods to measure such properties, the scope of this Phase I was to screen a vast number of combinations in a short period of time. The use of more rigorous methods (e.g., SEM, GC-MS, TGA, ICP) to determine surface compositions and to investigate the structure of the coating and products is within the scope of Phase II. Note that an enormous amount of time and money would have been spent evaluating the numerous powder and monomer/polymer combinations using more rigorous analytical methods, so our approach in Phase I did allow us to screen a large number of potential combinations at low cost and in a short period of time. Thermal activity in a DSC scan, indicating the presence of a phase other than the reactants, is a necessary observable IF any alteration (e.g., polymerization or formation of another organic) of the monomer or polymer has occurred as a result of contact with the metals. Now that the process and materials have been proven feasible, the use of more elaborate techniques to characterize the process and compounds involved will be much more cost effective.

The HPLC method was also selected to afford rapid turnaround, simplicity, statistical accuracy, and low cost. We are confident that the results from these tests are accurate and statistically significant since a detailed spike and recovery analysis was performed with the HPLC system for the simulants TDE and DMMP. Referring again to Figure 5, the absence of new peaks ***after*** the reaction with the DMMP or TDE may be explained by any one of the following: (1) the product(s) formed are adsorbed or immobilized by the substrate metal; (2) the product(s) formed are not soluble in the eluent; (3) the product(s) formed are gaseous at room temperature (e.g., CH_4, H_2S, CO_2); or (4) the product(s) formed do not absorb appreciably at wavelengths of 200-225 nm. This issue can not be resolved in the Phase I effort, but is one of the objectives of the Phase II effort.

Again, there are much more rigorous methods available but we chose to trade off this more detailed study with the ability to screen more metal alloy and monomer/polymer combinations and prove out the feasibility. More detailed analyses can now be pursued with a higher potential for success.

The selection of the simulants TDE and DMMP was based on our open literature review of simulants selected by other researchers and similarity in chemical structure to the CW agents.

There are numerous other possible simulants as discussed in literature including malathion, glyphosate, glyceraldehyde 3-phosphate, diazinon, bis(2-ethyl)phosphite, and di-isopropyl fluorophosphate for nerve agents, and 3,3'-thiodipropionic acid, dibutyl sulfide, di-*t*-butyl sulfide, and thioglycolic acid for sulfur mustard but the scope and funding of a Phase I effort only allows a reasonable number of compounds to be tested. Although some of these compounds may prove to be better simulants for certain tests, we selected the DMMP and TDE with the intent to mimic key functional groups and bonds, and electronic effects of nerve agents and sulfur mustard. The scope of Phase II will use additional simulants for completeness.

We also tested the synergism between the metal substrate and the polymer/monomer-derive coating. Independent tests contacting methyl methacrylate and propylene glycol butyl ether with DMMP and TDE showed no statistically significant reduction of the DMMP or TDE relative to the experimental results with the coated powders. Thus, we conclude that the neutralization or immobilization of the simulants is a result of other by-products formed and affixed to the metal alloy particles and/or the metal alloys themselves, the coating serving as an inert barrier or sealant. An organic barrier may be necessary, however, in a final formulation to protect the wearer from irritation and direct contact with the metal particles.

Overall, the $TiFe_{0.9}Mn_{0.1}H$/MM, $CaNi_5H_3$/PFP, and Mg_2NiH_2/PGBE combinations proved the most effective toward DMMP. The only commonality between all of these combinations is the hydride state of the metal alloy. Since the "oxide" analogs of these particular powder experiments were not tested via HPLC, it cannot be confirmed at the conclusion of this Phase I that the effectiveness is related to the hydrogen presence. The only oxides analyzed via HPLC were for the Mg_2Ni alloy with perfluoropropene. Since both the hydride and the oxide form of this reactant showed little or no significant immobilization or neutralization of DMMP or TDE, the oxide vs. hydride effect cannot be determined. A related observation is that considerable thermal activity strongly correlates with a hydrided metal substrate reacted with the monomer or polymer. If the immobilization or neutralization process is related to the same reaction mechanism which produces these observable thermal fingerprints, then the neutralization potential of the alloy with the simulants would correlate with the thermal activity (i.e., hydride form of the alloy).

CONCLUSIONS

Three metal alloys were selected, procured, activated, and decrepitated. The surface area for these powders typically ranges from 0.1-10 m^2/g, depending on the exact process variables used to prepare the powders. On average, the specific surface area of the powders is about 0.5-1 m^2/g. With a typical metallic density of about 6.6 g/cm^3, the particle diameter is estimated to be 0.9-1.8 μm (assuming spherical particles). After carrying out the metal activation and monomer/polymer reaction, the powder consistency ranged from dry and free-flowing to wet, sticky and clumpy, depending on the metal alloy and the monomer or polymer

Of the three metal alloys and 8 monomers or polymers studied, several showed thermal activity which could not be explained from the raw materials used. Of the combinations which exhibited above average thermal activity, we selected 6 combinations for CW agent simulant testing. Of these 6 materials, 3 combinations, listed below, produced a statistically significant neutralization or immobilization (20-100%) of the TDE and DMMP.

- $TiFe_{0.9}Mn_{0.1}H$ with methyl methacrylate (MM)
- Mg_2NiH_2 with propylene glycol butyl ether (PGBE)
- $CaNi_5H_3$ with perfluoropropene (PFP)

Of these combinations, two of the reactants were liquids at room temperature (MM and PGBE), and one was a vapor (PFP). This observation indicates that there is no apparent favorable reaction phase for the metal alloys. *(NOTE: These materials have also been submitted to the U.S. Army Medical Research Institute of Chemical Defense for testing in barrier cream formulations).* The statistical significance of simulant neutralization/immobilization by these substrates was determined at 95% confidence following standard ANOVA procedures. This method used a comparison of F-values between two 15-20 sample lots of the organic-coated and raw material metal alloy.

We also tested the synergism between the metal substrate and the polymer/monomer-derive coating. Independent tests contacting methyl methacrylate and propylene glycol butyl ether with DMMP and TDE showed no statistically significant reduction of the DMMP or TDE relative to the experimental results with the coated powders. Thus, we conclude that the neutralization or immobilization of the simulants is a result of other by-products formed and affixed to the metal alloy particles and/or the metal alloys themselves, the coating serving as an inert barrier or sealant.

The Phase I experiments also determined that the variables having the greatest influence in producing "thermal activity" were the monomer or polymer reactant, and whether the alloy was left in a hydrided form prior to reacting with the monomer or polymer. We correlate this activity to the degree of success in forming organic products on the metal surface which have different physical properties than the reactant monomer or polymers. The hydride effect was hypothesized prior to the experiments since monatomic H (in the form of H^+ or free-radical H) will be present near or at the surface of the metal during desorption and absorption, and available as a possible

source to fuel polymerization or reduction reactions. We can only speculate at this stage in the research that the thermal activity may be correlated to a neutralization or immobilization potential assuming that the monomer or polymer reaction mechanism would be related the neutralization/immobilization mechanism.

From the success of the limited scope Phase I effort, we suspect that other combinations of metal alloys and monomers or polymers studied in Phase I would also be found effective against CW agents. To appreciate and understand the fundamental mechanism of immobilization and the full potential of these novel metal alloys substrates in skin protection, a much more in-depth research effort is required.

We conclude that both the powder activation/preparation process and the use of these powders as skin protectants are not only feasible, but successful. We have established a statistical significance of CW agent simulant neutralization or immobilization for several metal and polymer combinations from only a select pool of candidates. These compounds could also function in a chromatographic capacity within barrier cream formulations (similar to the currently used Teflon particles), in addition to catalytically neutralizing or destructively adsorbing the CW agents. In particular, and per Task 6 in the proposal, one improved formulation might consist of the $TiFe_{0.9}Mn_{0.1}$/MM powder and the Mg_2NiH_2/PGBE powder, although the $TiFe_{0.9}Mn_{0.1}H$/MM powder may be effective against both DMMP and TDE alone. Any chromatographic effects would have to verified and optimized in actual barrier cream formulations.

A brief economic analysis for the $TiFe_{0.9}Mn_{0.1}$/MM powder is illustrated below. On a per kg of $TiFe_{0.9}Mn_{0.1}$ basis, the costs are: \$300/kg for the $TiFe_{0.9}Mn_{0.1}$ raw material, approximately (\$6/L methyl methacrylate) x (1 kg $TiFe_{0.9}Mn_{0.1}$/L MM) = \$6/kg $TiFe_{0.9}Mn_{0.1}$, and (\$0.013/L_{STP} H_2) x (470 L_{STP} H_2/kg $TiFe_{0.9}Mn_{0.1}$) = \$6/kg $TiFe_{0.9}Mn_{0.1}$. The hydrogen consumption is estimated assuming 10 fully-hydrided cycles to decrepitate the powder with 20% loss per cycle. Note that the H_2 can be recycled between two or more equally sized beds with one bed absorbing while the other is heated and desorbing: the 20% loss assumes not all of the H_2 can be shuttled efficiently between the beds. The total product materials cost would then be \$300+6+6=\$312 of which 96% is attributed to the $TiFe_{0.9}Mn_{0.1}$ material costs.

Since positive results were measured with only a limited pool of materials in this Phase I effort, there is a strong likelihood that these or even better skin protectant formulations could be identified from a larger pool of candidates in continuing research. Continuing research will also reveal the mechanism of the neutralization or immobilization processes shedding light on the potential of these compounds in other commercial and military applications.

REFERENCES

PATENTS

1. Altemore, M., and Ort, M.R., "Polymerization of ethylene," US patent 3,899,477 (1975).
2. Back, D.D., and Ramos, C., "Method for the destruction of heteroatom organics using transition-alkaline-rare earth metal alloys," patent pending.
3. Bannard, R.A.B., et al., "Chemical warfare agent decontaminant composition containing an alkali metal salt of oximes, phenol, or PEG monoethers," GB patent 2,239,598 (1991).
4. Bannard, R.A.B., et al., "Metal phenoxide/polyethylene glycols for protecting the body from chemical warfare agents," Canadian patent 1,321,949 (1993).
5. Bannard, R.A.B., et al., "Phenol or oxime salt-containing protective composition against chemical warfare agents," GB patent 2,237,739 (1991).
6. Braude, G.L., and Lard, E.W., "Laminates from a fabric coated with binder and pulverulent molecular sieve for protection against organophosphorous poisons," US patent 3,431,133 (1969).
7. Dahms, G.H., "Sunscreen composition containing metal oxide dispersed in oil," EP patent 628,303 (1994).
8. Hart, J.A.H., "cellular resin foams resistant to the passage of noxious chemicals in liquid and vapor form," CA patent 878,560 (1971).
9. Miro, N.D., "Olefin polymerization process for preparing high density or linear low density polymers of controlled molecular weight distribution," US patent 4,972,033 (1990).
10. Murphy R.T., and Lajoie, M.S., "Cosmetics containing hydrophilic polymer-coated microcrystallites of bicarbonate salt," US patent 5,482,702 (1996).
11. Sasaki, Y., and Saitoh, I., "Skin protecting composition comprising silicone-acrylic copolymers," EP 391,273 (1990).
12. Sasaki, Y., and Saitoh, I., "Skin protective composition comprising an acrylic copolymer," EP 391,274 (1990).
13. Steyermark, P.R., "Decontaminating chemical warfare agents," US patent 3,810,788 (1974).
14. Ziegler, K., et al., "Polymerization of ethylenically unsaturated hydrocarbons," US patent 4,063,009 (1977).

JOURNALS, REPORTS, OTHER

1. Back, D.D., "Hydride-Synthesized High Surface Area Metal Oxide Powders," Phase I SBIR Final Report, September 1995.
2. Back, D.D., et al., "Highly destructive polymer-contained neutralizing skin protectants," SBIR Phase I Monthly Technical Reports #1, #2, #3, #4, and $#5, Dec. 1996-April 1997.

3. Berg, F.J., et al., "Cleavage of phenylphosphonothioates by hydroxide ion and by micellar iodosobenzoate," Langmuir, v 11 n 2, p 411-13, 1995.

4. Blank, M.R., "Survey: destruction of chemical agent simulants in supercritical water oxidation," DTIC report A258-206 (1992).

5. Bruk, M.A., and Kirpikov, S.V., "A method for encapsulation of powders by vapor-phase polymerization," Colloid J., v 57 n 2, p 160-5, 1995.

6. Cataldo, D.A., et al., "Acute ecological toxicity and environmental persistence of simulants," NTIS report DE88014762 (1988).

7. Copa, W.M., and Momont, J.A., "Wet air oxidation of energetics and chemical agent surrogates," J. Energ. Mater., v 13 n 3&4, p 235-58, 1995.

8. Davis, F.A., et al., "beta-(N,N-dialkylamino)ethyl arylthiosulfonates: new simulants for O-ethyl S-[2-(diisopropylamino)ethyl] methylphosphonothioate," J. Org. Chem., v 57 n 9, p 2594-9, 1992.

9. Gruber, W., "Ultrafine Metal Oxides Dismantle Chlorinated Organics," Environ. Eng. World, p 36, July-August 1995.

10. Hammond, P.S., and Forster, J.S., "A polymeric amine-copper(II) complex as catalyst for the hydrolysis of Soman and DFP," J. Appl. Polymer Sci., v 43 n 10, p 1925-31, 1991.

11. Jabloska, B., "Usability of plastic coated fabrics for cloth protecting against liquid pesticides," Pr. Cent. Instr. Ochr. Pr., v 21 n 69, p 105-14, 1971.

12. Klabunde, K.J., Activated Metal Oxide Surfaces as Highly Basic and Reducing Environments, Final Report contract DAAG29-84-K-0051, U.S. Army Research Office, RTP, NC, 1987. (AD-A184-958)

13. Klabunde, K.J., Activated Metal Oxide Surfaces as Highly Reactive Environments, Final Report contract DAAL03-87-K-0130, U.S. Army Research Office, RTP, NC, 1990. (AD-A227-990)

14. Klabunde, K.J., and Matsuhashi, H., A Comparison of Electron Donor and Proton Abstraction Activities of Thermally Activated Pure Magnesium Oxide and Doped Magnesium Oxides, J. Am. Chem. Soc., 109(4), p1111, 1987.

15. Koper, O., Yong, X.L., and Klabunde, K.J., Destructive Adsorption of Chlorinated Hydrocarbons on Ultrafine (Nanoscale) Particles of Calcium Oxide, Chem. Mater., 5(4), p500, 1993. (A282-250)

16. Leslie, D.R., and Ward, J.R., "Metal-ion catalyzed oxidation of a G-agent simulant by oxone," DTIC report A254-351 (1992).

17. Matsumura, H., and Nakabayashi, N., "Adhesive 4-META/MMA-TBB opaque resins with poly(methyl methacrylate)-coated titanium dioxide," J. Dent. Res., v 67 n 1, p 29-32, 1988.

18. Ono, T., and Takahashi, T., "Preparation of powdery metal -organic polymer composite materials," Kenkyu Kiyo-MKKSG, v 25, p 107-14, 1989.

19. Pal, T., et al., "Permeation measurements of chemical agent simulants through protective clothing," J. Hazard. Mater., v 33 n 1, p 123-41, 1993.

20. Reifenrath, W.G., "Evaluation of animal models predicting skin penetration in man," Fundam. Appl. Toxicol., v 4 n 2, p 224-30, 1984.

21. Revelle, J.B., "The Two-Day Statistician, An Introduction to Statistical Quality Control," training seminar by Hughes Aircraft Co., 1990.

22. Sawyer, T.W., et al., "Efficacy of an oximate-based skin decontaminant against organophosphate nerve agents determined in vivo and in vitro," Toxicology, 67, pgs 267-77, 1991.

23. Ulrich, H., "Introduction to Polymers," 2nd edition, Carl Hanser Verlag, Munich, 1993.

24. Yamaguchi, T., et al., "Coating of metal powder surface with poly(methyl methacrylate)," Chem. Ind., v 17, p 748, 1975.

25. Yong, X.L., and Klabunde, K.J., Nanoscale Metal Oxide Particles as Chemical Reagents. Destructive Adsorption of a Chemical Agent Simulant, Dimethyl Methylphosphonate, on Heat-Treated Magnesium Oxide, Langmuir, 7, p1388, 1991. (A249-303)

26. Yong, X.L., Koper, O., Atteya, M., and Klabunde, K.J., Adsorption and Decomposition of Organophosphorous Compounds on Nanoscale Metal Oxide Particles. In Situ GC-MS Studies of Pulsed Microreactions over Magnesium Oxide, Chem. Mater., 4, p323, 1992. (A254-475)

BIBLIOGRAPHY OF PUBLICATIONS

No publications have been submitted to date for the research of this effort.

MEETING ABSTRACTS

A Phase I review meeting per Task 5 was held at Mainstream Engineering Corporation in Rockledge, Fl, on may 15, 1997. In attendance were Dr. Dwight D. Back and Dr. Robert P. Scaringe of Mainstream Engineering, and Maj. Alan F. Weir and Maj. Erich K. Lehnert of the U.S. Army Medical Research Institute of Chemical Defense. Dr. Back reviewed the Phase I SBIR effort technical approach and results, and gave a facility tour and demonstration of the apparatus used for the project. Maj. Alan F. Weir and Maj. Erich K. Lehnert also suggested that the powders be tested in a barrier cream formulation and Dr. Back agreed to prepare and send a finer scale powder to the U.S. Army Medical Research Institute of Chemical Defense for formulation. Maj. Alan F. Weir and Maj. Erich K. Lehnert agreed to check with their contracting office about extending the submission time for the Phase II proposal so as to allow Mainstream time to incorporate any efficacy results measured for the powder formulations.

LIST OF PERSONNEL

The Mainstream Engineering Corporation personnel who worked on this research effort are:

- Dwight D. Back, Senior Chemical Engineer
- John A. Meyer, Research Scientist
- Charlie Ramos, Chemical Engineer/Laboratory Manager
- Steven Jezowski, Welder/Machinist
- William Rhodes, Sheet Metal Mechanic

No other personnel outside of Mainstream were active on this contract.

This document contains [redacted]PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the expressed written permission of Mainstream.

APPENDICES

Appendix A - Experimental Matrices

Appendix B - ANOVA Results of Experimental Matrices

Appendix C - DSC Scan Raw Data

Appendix D - HPLC Raw Data and Statistics

This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the expressed written permission of Mainstream.

APPENDIX A - EXPERIMENTAL MATRICES

TABLE A-1:

OXIDE POLYMERIZATION EXPERIMENTS - 25 g $CaNi_5$

PURPOSE: Determine the polymerization potential of $CaNi_5O_x$ powder with methyl methacrylate and perfluoropropene monomers at 2 pressure levels and 2 temperature levels. Analyze via LC for simulant neutralization potential if polymerized product detected via DSC.

exp't	monomer	reaction T (C)	monomer P (psia)
CaNi-1(O)	Methyl Methacrylate	25	10
CaNi-2(O)	Methyl Methacrylate	100	150
CaNi-3(O)	Perfluoropropene	25	150
CaNi-4(O)	Perfluoropropene	100	10

TABLE A-2:

HYDRIDE POLYMERIZATION EXPERIMENTS - 25 g $CaNi_5$

PURPOSE: Determine the polymerization potential of $CaNi_5H_3$ powder with methyl methacrylate and perfluoropropene monomers at 2 pressure levels and 2 temperature levels. Analyze via LC for simulant neutralization potential if polymerized product detected via DSC.

exp't	monomer	reaction T (C)	monomer
CaNi-5(H)	Methyl Methacrylate	35	~0.26 moles, LIQ
CaNi-6(H)	Methyl Methacrylate	100	~0.26 moles, LIQ
CaNi-7(H)	Perfluoropropene	35	~0.26 moles, VAP
CaNi-8(H)	Perfluoropropene	100	~0.26 moles, VAP

TABLE A-3:

OXIDE POLYMERIZATION EXPERIMENTS - 25 g $TiFe_{0.9}Mn_{0.1}$

PURPOSE: Determine the polymerization potential of $TiFe_{0.9}Mn_{0.1}O_x$ powder with methyl methacrylate and perfluoropropene monomers at 2 pressure levels and 2 temperature levels. Analyze via LC for simulant neutralization potential if polymerized product detected via DSC.

exp't	monomer	reaction T (C)	monomer P (psia)
TiFeMn-1(O)	Methyl Methacrylate	25	10
TiFeMn-2(O)	Methyl Methacrylate	100	150
TiFeMn-3(O)	Perfluoropropene	25	150
TiFeMn-4(O)	Perfluoropropene	100	10

TABLE A-4:

HYDRIDE POLYMERIZATION EXPERIMENTS - 25 g $TiFe_{0.9}Mn_{0.1}$

PURPOSE: Determine the polymerization potential of $TiFe_{0.9}Mn_{0.1}H$ powder with methyl methacrylate and perfluoropropene monomers at 2 pressure levels and 2 temperature levels. Analyze via LC for simulant neutralization potential if polymerized product detected via DSC.

exp't	monomer	reaction T (C)	monomer
TiFeMn-5(H)	Methyl Methacrylate	35	~0.26 moles, LIQ
TiFeMn-6(H)	Methyl Methacrylate	100	~0.26 moles, LIQ
TiFeMn-7(H)	Perfluoropropene	35	~0.26 moles, VAP
TiFeMn-8(H)	Perfluoropropene	100	~0.26 moles, VAP

This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the expressed written permission of Mainstream.

TABLE A-5:

OXIDE POLYMERIZATION EXPERIMENTS - 25 g Mg_2Ni

PURPOSE: Determine the polymerization potential of Mg_2NiO_x powder with methyl methacrylate and perfluoropropene monomers at 2 pressure levels and 2 temperature levels. Analyze via LC for simulant neutralization potential if polymerized product detected via DSC.

exp't	monomer	reaction T (C)	monomer P (psia)
MgNi-1(O)	Methyl Methacrylate	25	10
MgNi-2(O)	Methyl Methacrylate	100	150
MgNi-3(O)	Perfluoropropene	25	150
MgNi-4(O)	Perfluoropropene	100	10

TABLE A-6:

HYDRIDE POLYMERIZATION EXPERIMENTS - 25 g Mg_2Ni

PURPOSE: Determine the polymerization potential of Mg_2NiH_2 powder with methyl methacrylate and perfluoropropene monomers at 2 pressure levels and 2 temperature levels. Analyze via LC for simulant neutralization potential if polymerized product detected via DSC.

exp't	monomer	reaction T (C)	monomer
MgNi-5(H)	Methyl Methacrylate	35	~0.26 moles, LIQ
MgNi-6(H)	Methyl Methacrylate	100	~0.26 moles, LIQ
MgNi-7(H)	Perfluoropropene	35	~0.26 moles, VAP
MgNi-8(H)	Perfluoropropene	100	~0.26 moles, VAP

This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the expressed written permission of Mainstream.

TABLE A-7:

DIRECT LIQUID CONTACTING EXPERIMENTS

PURPOSE: Determine the polymerization and simulant neutralization potential of various metal alloys with 3 polymer liquids and 1 monomer liquid using a direct liquid contacting (DLC) method.

exp't	metal	liquid
DLC-1	CaNi5-oxide	poly(dimethylsiloxane)
DLC-2	Mg2Ni-hydride	poly(dimethylsiloxane) + 5% water
DLC-3	TiFeMn-oxide	poly(dimethylsiloxane) + 5% water
DLC-4	Mg2Ni-hydride	poly(ethylene glycol) + 5% water
DLC-5	TiFeMn-oxide	poly(ethylene glycol) + 5% water
DLC-6	Mg2Ni-hydride	PEG methyl ether
DLC-7	Mg2Ni-oxide	PEG methyl ether
DLC-8	Mg2Ni-hydride	propylene glycol butyl ether

This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

APPENDIX B - ANOVA Results of Experimental Matrices

$CaNi_5$ Oxide

DATE: 04/22/97

	factor 1	*factor 2*	*factor 3*	
EXP'T	**monomer**	**reaction T (C)**	**monomer P (psia)**	**DSC response**
1	MM	25	10	0
2	MM	100	150	0
3	PFP	25	150	0
4	PFP	100	10	0

monomer	**factor 1**	MM	0
		PFP	0
		EFFECT	**0**

reaction T (C)	**factor 2**	25	0
		100	0
		EFFECT	**0**

monomer P (psia)	**factor 3**	10	0
		150	0
		EFFECT	**0**

$CaNi_5$ Hydride

DATE: 04/22/97

	factor 1	*factor 2*	*factor 3*	
EXP'T	**monomer**	**reaction T (C)**	**monomer P (psia)**	**DSC response**
5	MM	25	10	1
6	MM	100	150	1
7	PFP	25	150	1
8	PFP	100	10	0

monomer	**factor 1**	MM	1
		PFP	0.5
		EFFECT	**0.5**

reaction T (C)	**factor 2**	25	1
		100	0.5
		EFFECT	**0.5**

monomer P (psia)	**factor 3**	10	0.5
		150	1
		EFFECT	**0.5**

Mg_2Ni Oxide

DATE: 04/22/97

	factor 1	*factor 2*	*factor 3*	
EXP'T	**monomer**	**reaction T (C)**	**monomer P (psia)**	**DSC response**
1	MM	25	10	0
2	MM	100	150	0
3	PFP	25	150	15
4	PFP	100	10	15

monomer	**factor 1**	MM	0
		PFP	15
		EFFECT	**15**
reaction T (C)	**factor 2**	25	7.5
		100	7.5
		EFFECT	**0**
monomer P (psia)	**factor 3**	10	7.5
		150	7.5
		EFFECT	**0**

Mg_2Ni Hydride

DATE: 04/23/97

	factor 1	*factor 2*	*factor 3*	
EXP'T	**monomer**	**reaction T (C)**	**monomer P (psia)**	**DSC response**
5	MM	25	10	22
6	MM	100	150	17
7	PFP	25	150	17
8	PFP	100	10	16

monomer	**factor 1**	MM	19.5
		PFP	16.5
		EFFECT	**3**

reaction T (C)	**factor 2**	25	19.5
		100	16.5
		EFFECT	**3**

monomer P (psia)	**factor 3**	10	19
		150	17
		EFFECT	**2**

$TiFe_{0.9}Mn_{0.1}$ Oxide

DATE: 04/22/97

	factor 1	*factor 2*	*factor 3*	
EXP'T	**monomer**	**reaction T (C)**	**monomer P (psia)**	**DSC response**
1	MM	25	10	0
2	MM	100	150	0
3	PFP	25	150	0
4	PFP	100	10	0

monomer	**factor 1**	MM	0
		PFP	0
		EFFECT	**0**

reaction T (C)	**factor 2**	25	0
		100	0
		EFFECT	**0**

monomer P (psia)	**factor 3**	10	0
		150	0
		EFFECT	**0**

$TiFe_{0.9}Mn_{0.1}$ Hydride

DATE: 04/23/97

	factor 1	*factor 2*	*factor 3*	
EXP'T	**monomer**	**reaction T (C)**	**monomer P (psia)**	**DSC response**
5	MM	25	10	11
6	MM	100	150	11
7	PFP	25	150	0
8	PFP	100	10	1

monomer	**factor 1**	MM	11
		PFP	0.5
		EFFECT	**10.5**
reaction T (C)	**factor 2**	25	5.5
		100	6
		EFFECT	**0.5**
monomer P (psia)	**factor 3**	10	6
		150	5.5
		EFFECT	**0.5**

This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

APPENDIX C - DSC SCANS FOR REACTED METAL POWDERS

- CaNi-1 through CaNi-4
- CaNi-5 through CaNi-8
- MgNi-1 through MgNi-4
- MgNi-5 through MgNi-8
- TiFeMn-1 through TiFeMn-4
- TiFeMn-5 through TiFeMn-8
- DLC-1 through DLC-8
- poly(ethylene glycol)
- poly(ethylene glycol) methyl ether
- propylene glycol butyl ether
- poly(methylsiloxane)

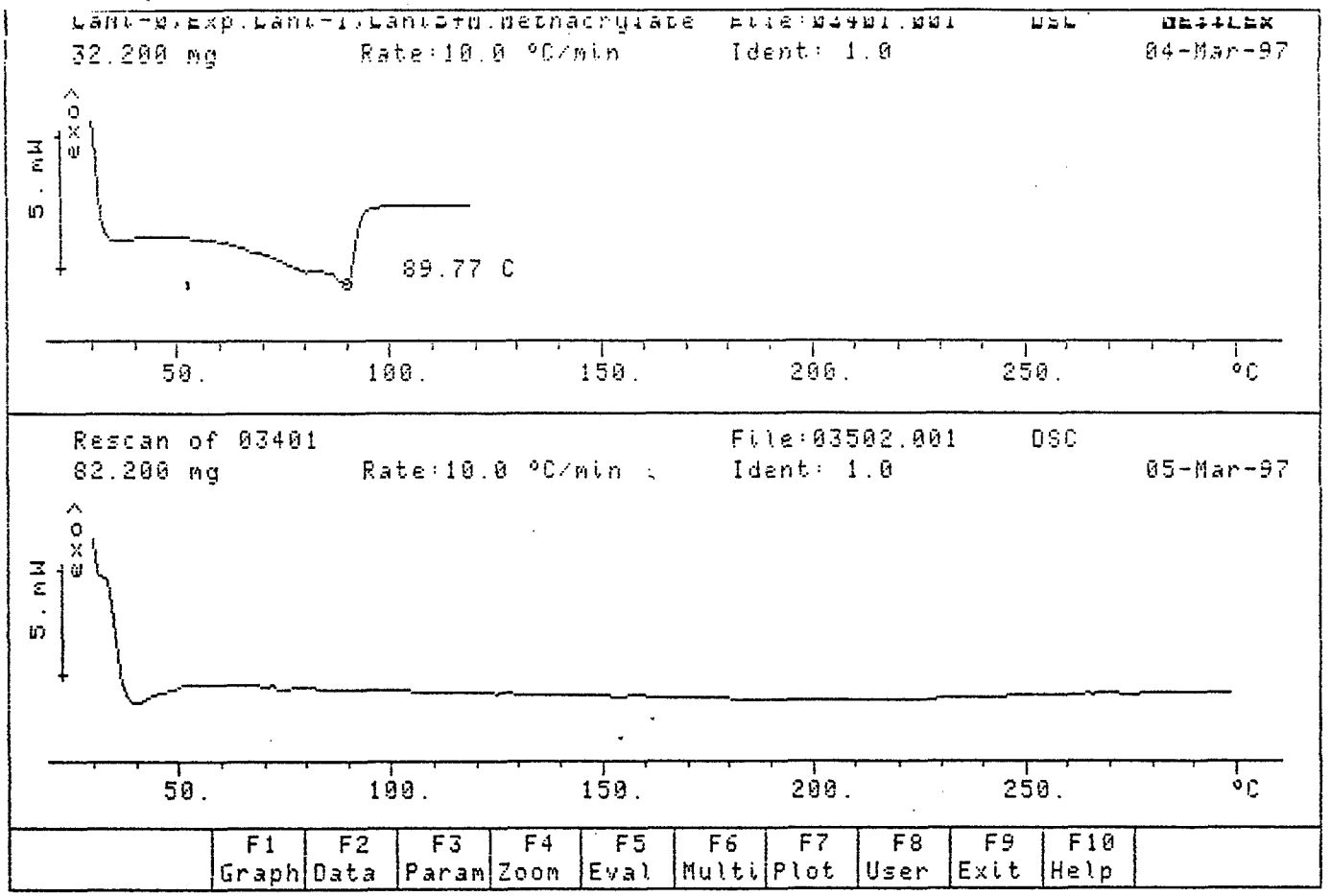
and the following scans for finer-scale powder materials sent to the U.S. Army Medical Research Institute for Chemical Defense:

- CaNi-H (fine)
- CaNi-8 (fine)
- MgNi-H (fine)
- DLC-8 (fine)
- TiFeMn-H (fine)
- TiFeMn-5 (fine)

CaNi-1

CaNi5 & Methyl

Methacrylate

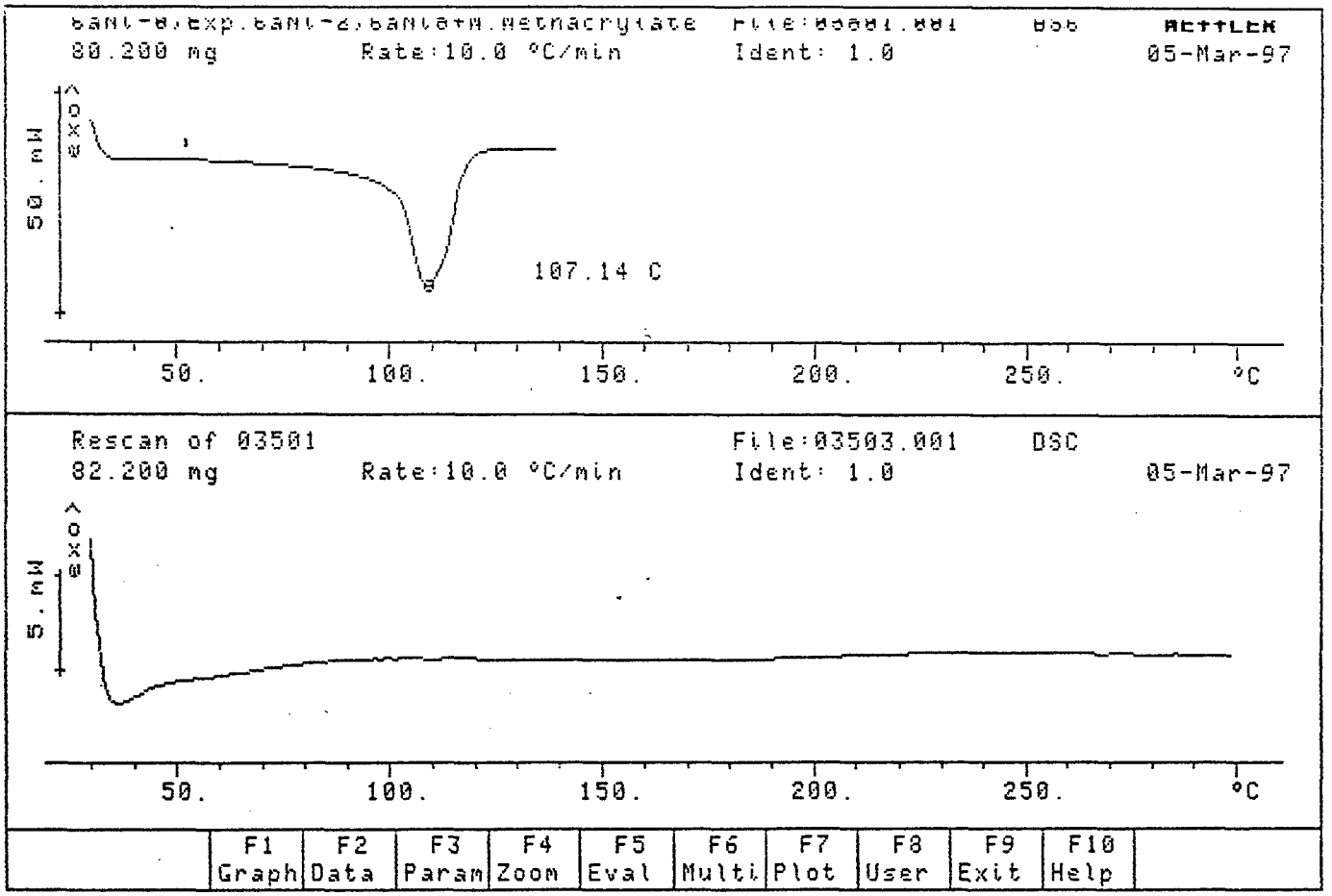


This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

CaNi-2

CaNi5 & Methyl

Methacrylate

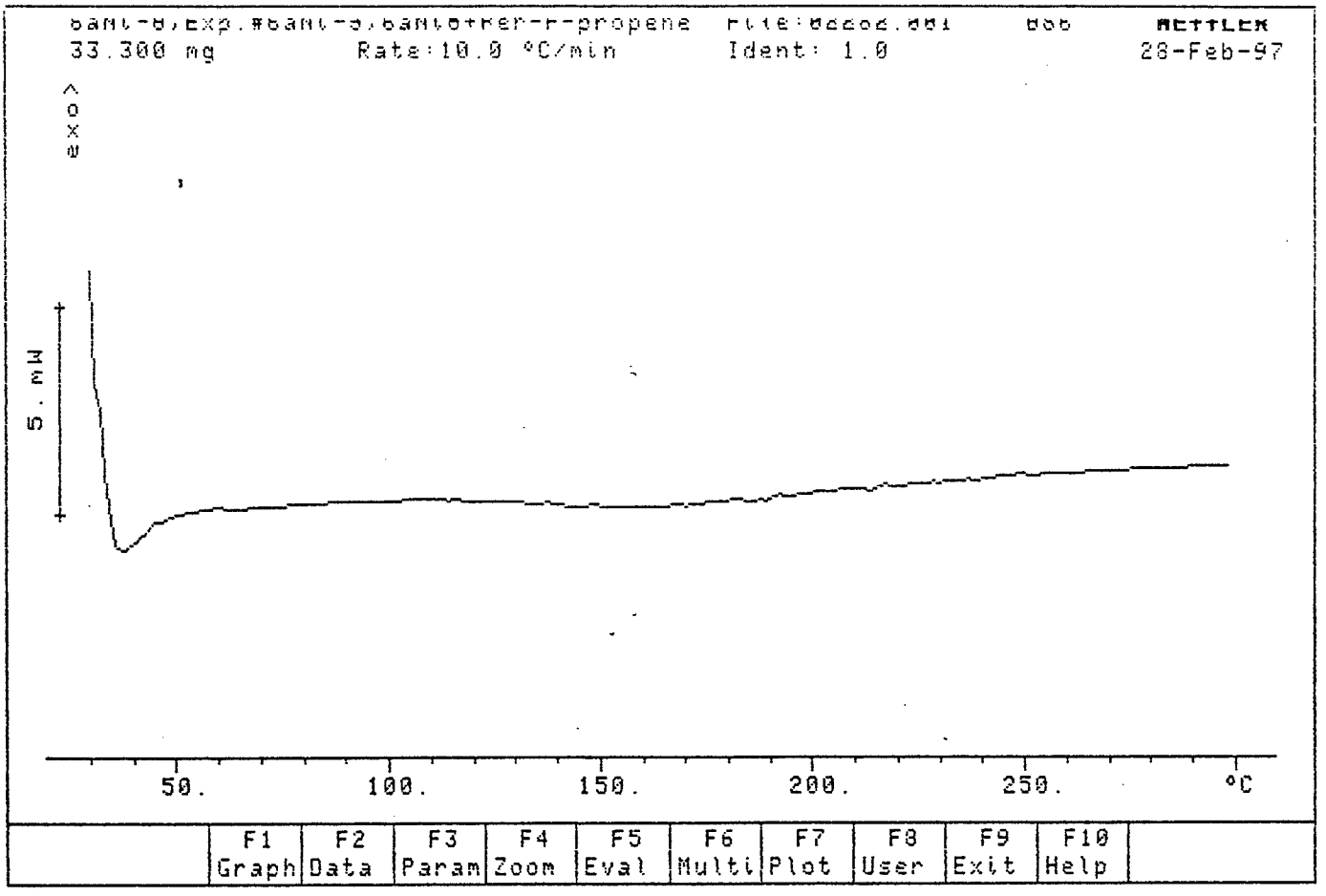


This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be duplicated or disclosed, in whole or in part, except with the written permission of Mainstream.

CaNi-3

CaNi5 &

Perfluropropene

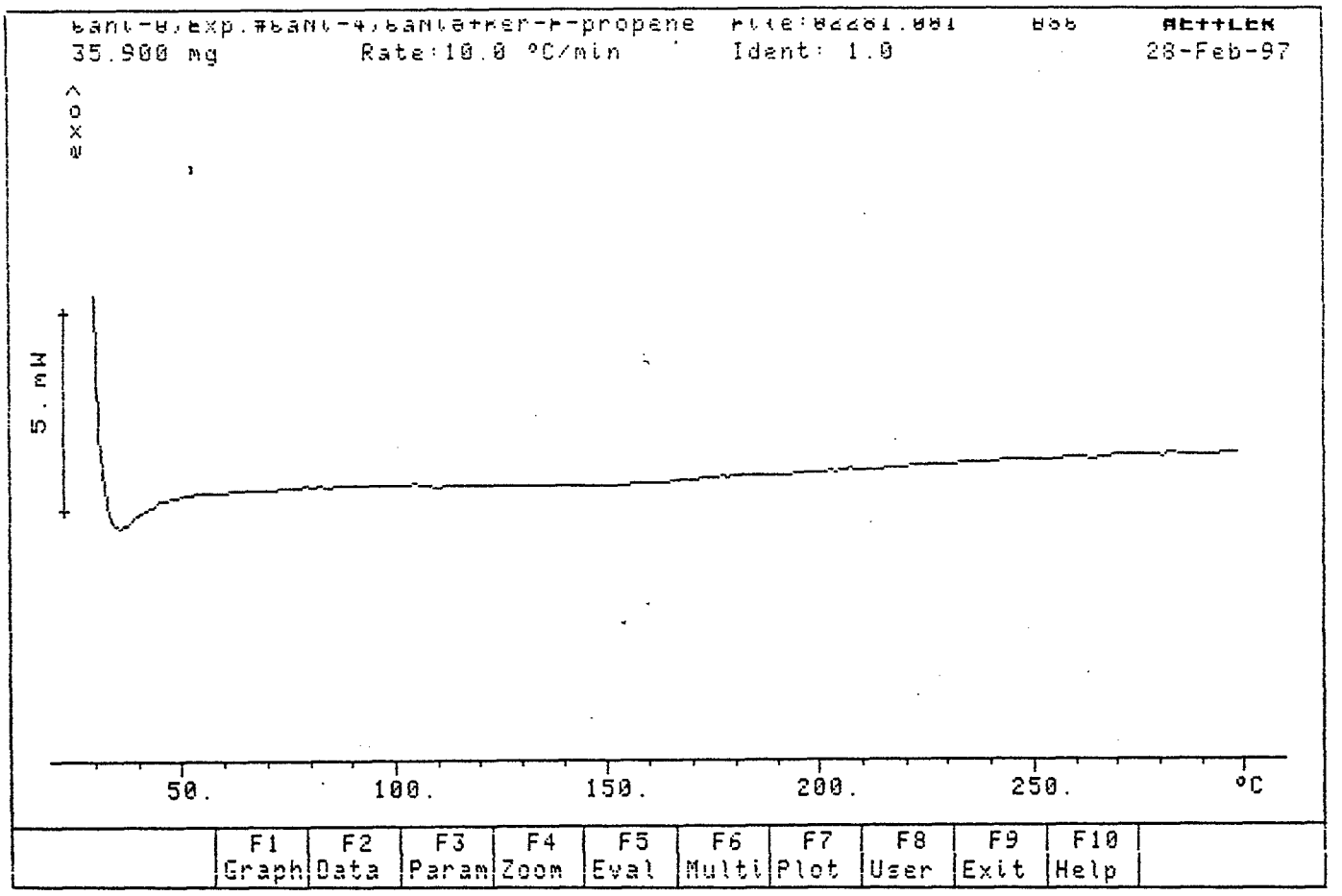


This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

CaNi-4

CaNi5 &

Perfluropropene

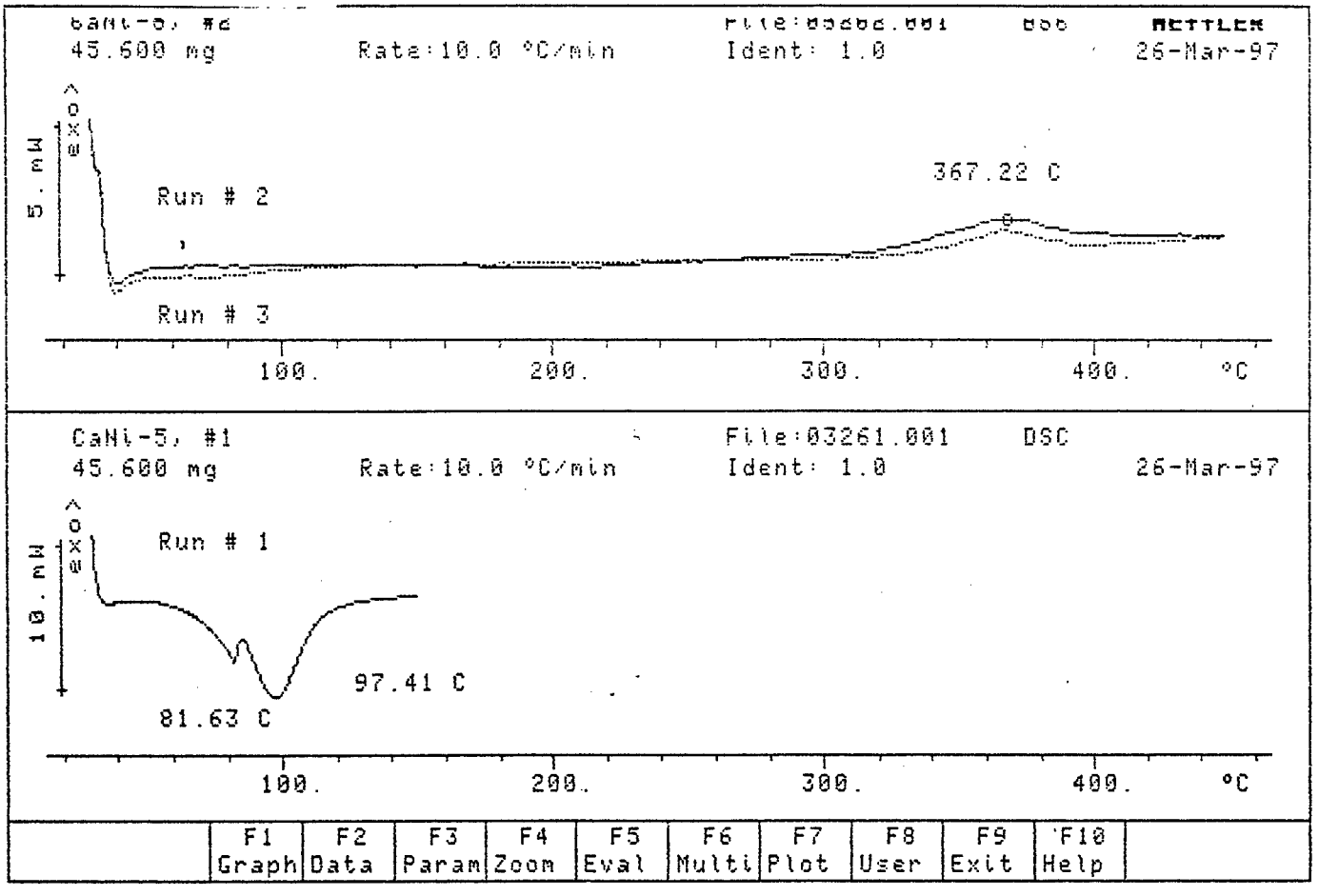


This document contains CONFIDENTIAL and PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

CaNi-5

CaNi5 & Methyl

Methacrylate

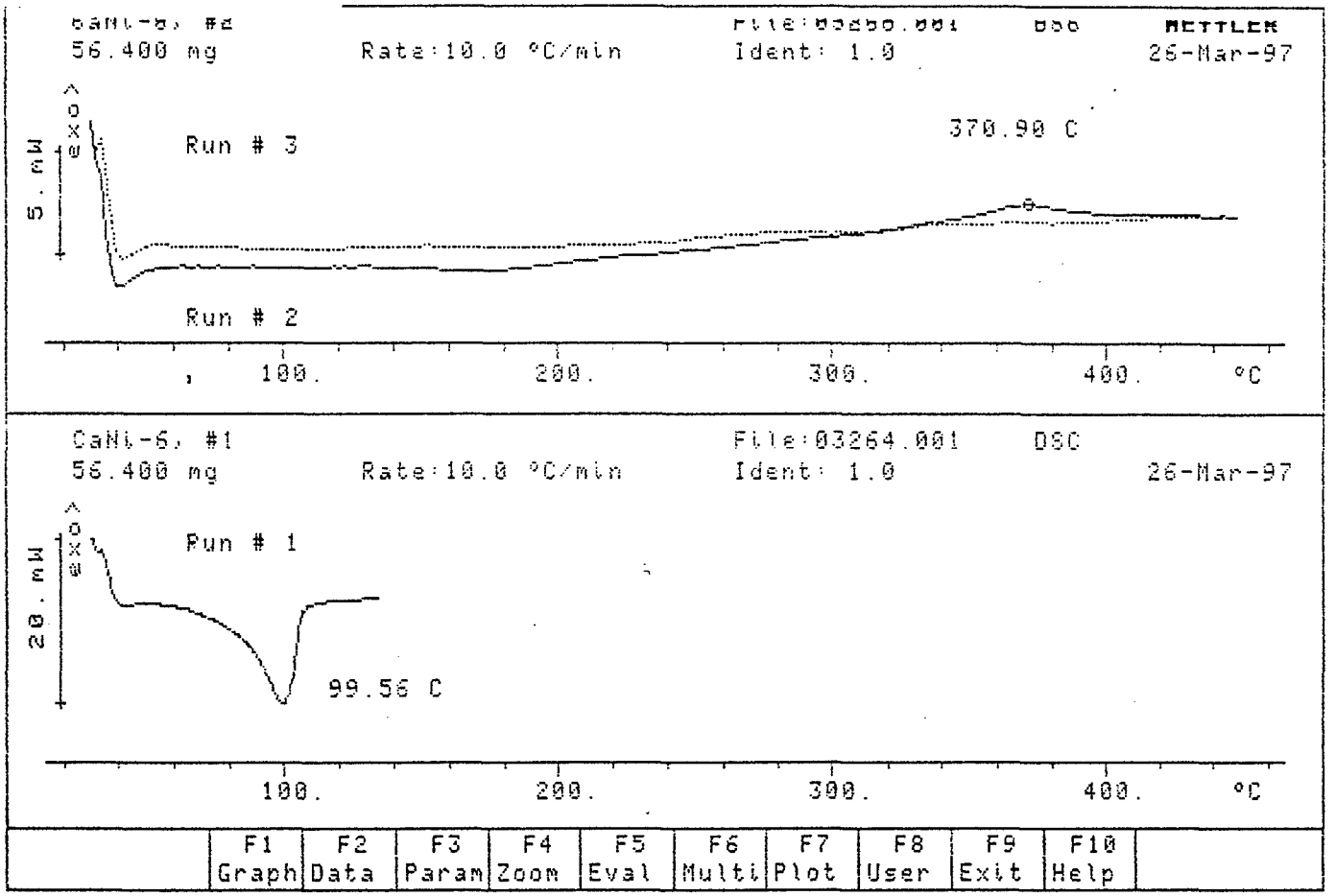


document contains CONFIDENTIAL and PROPRIETARY
of Mainstream Engineering Corporation and cannot be
duplicated or disclosed, in whole or in part, except with the
written permission of Mainstream.

CaNi-6

CaNi5 & Methyl

Methacrylate

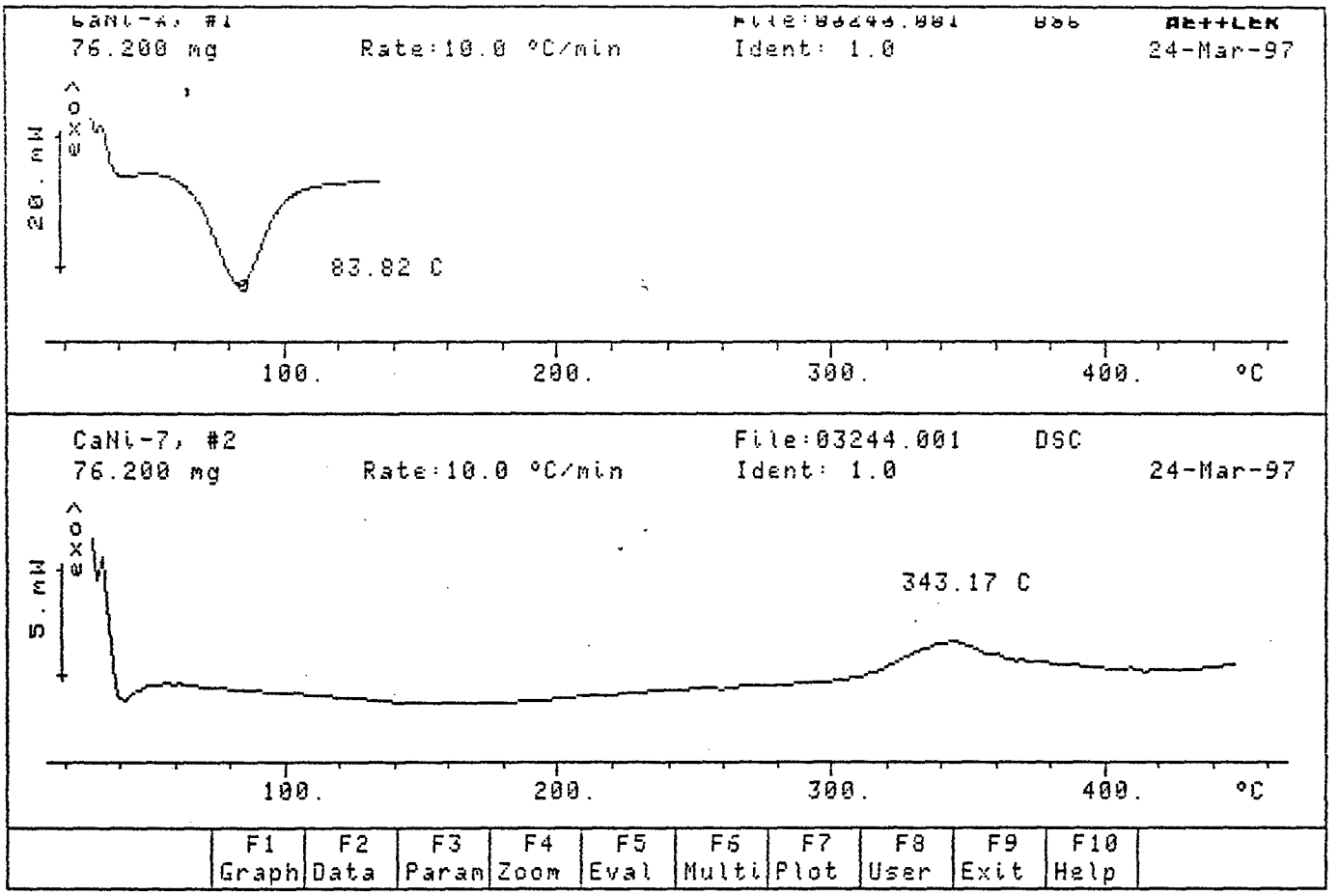


document contains CONFIDENTIAL and PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

CaNi-7

CaNi5 &

Perfluoropropene

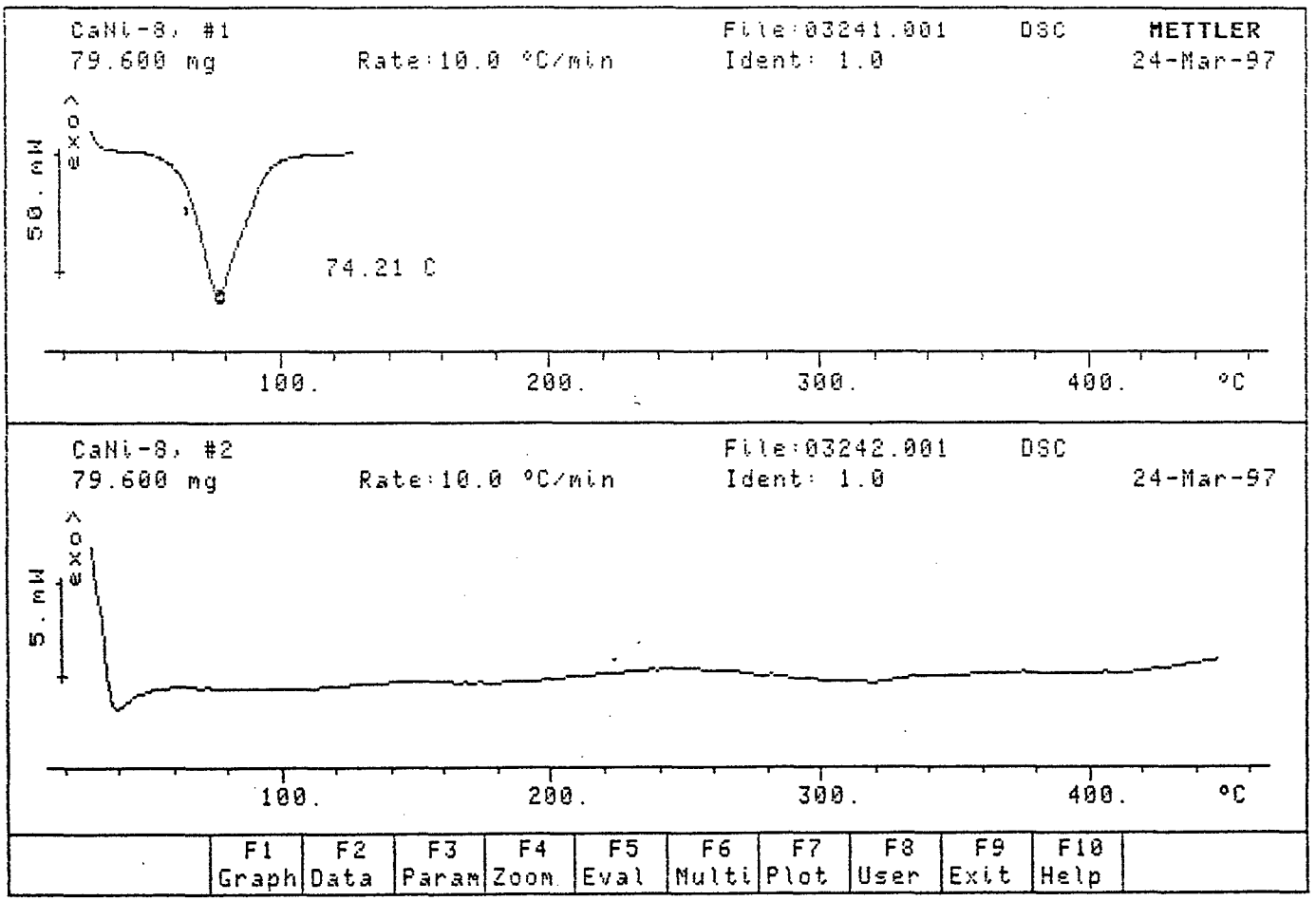


document contains [redacted] and PROPRIETARY
tion of Mainstream Engineering Corporation and cannot be
uplicated or disclosed, in whole or in part, except with the
ns written permission of Mainstream.

CaNi-8

CaNi5 &

Perfluoropropene

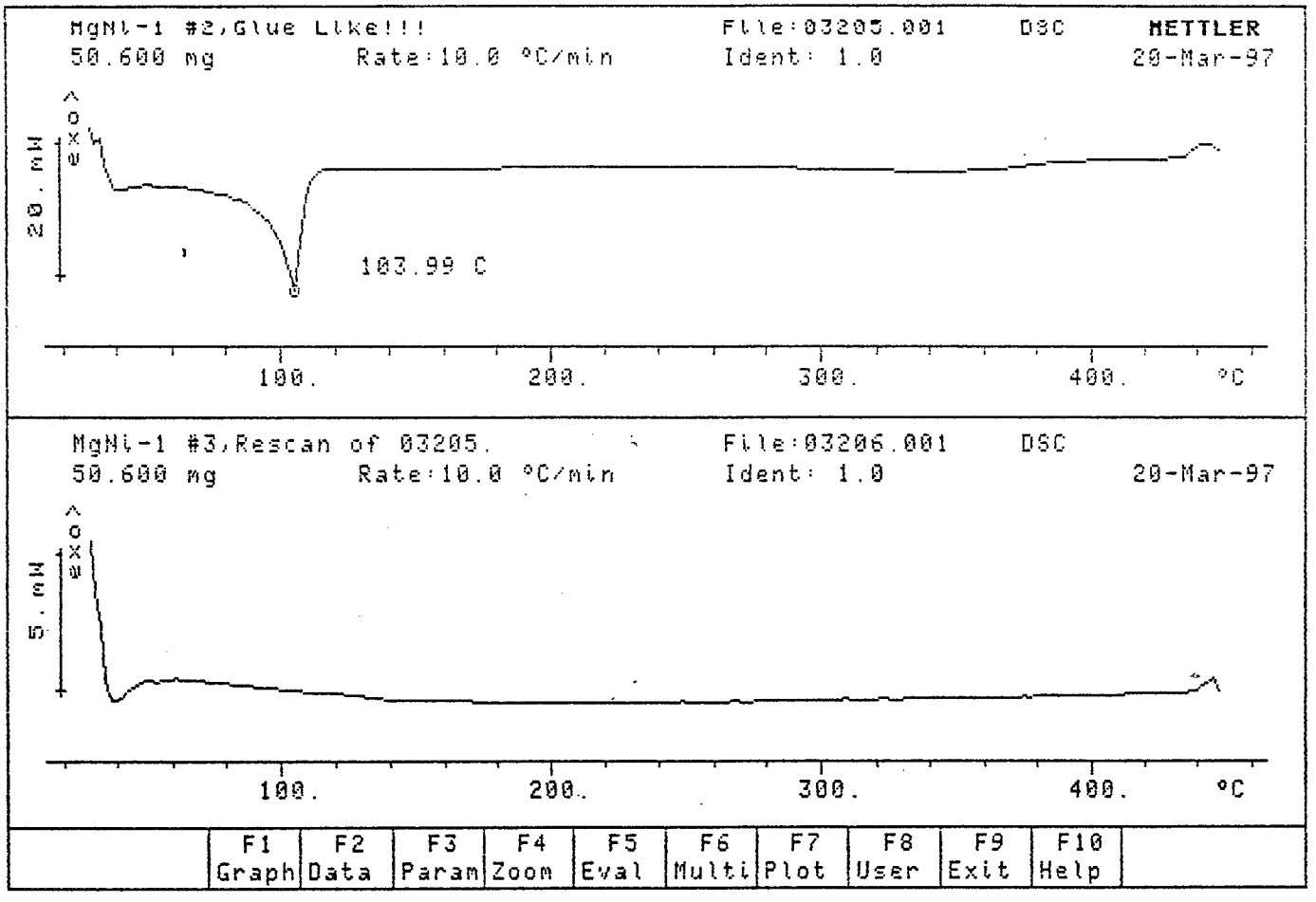


Document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

MgNi-1

Mg2Ni & Methyl

Methacrylate

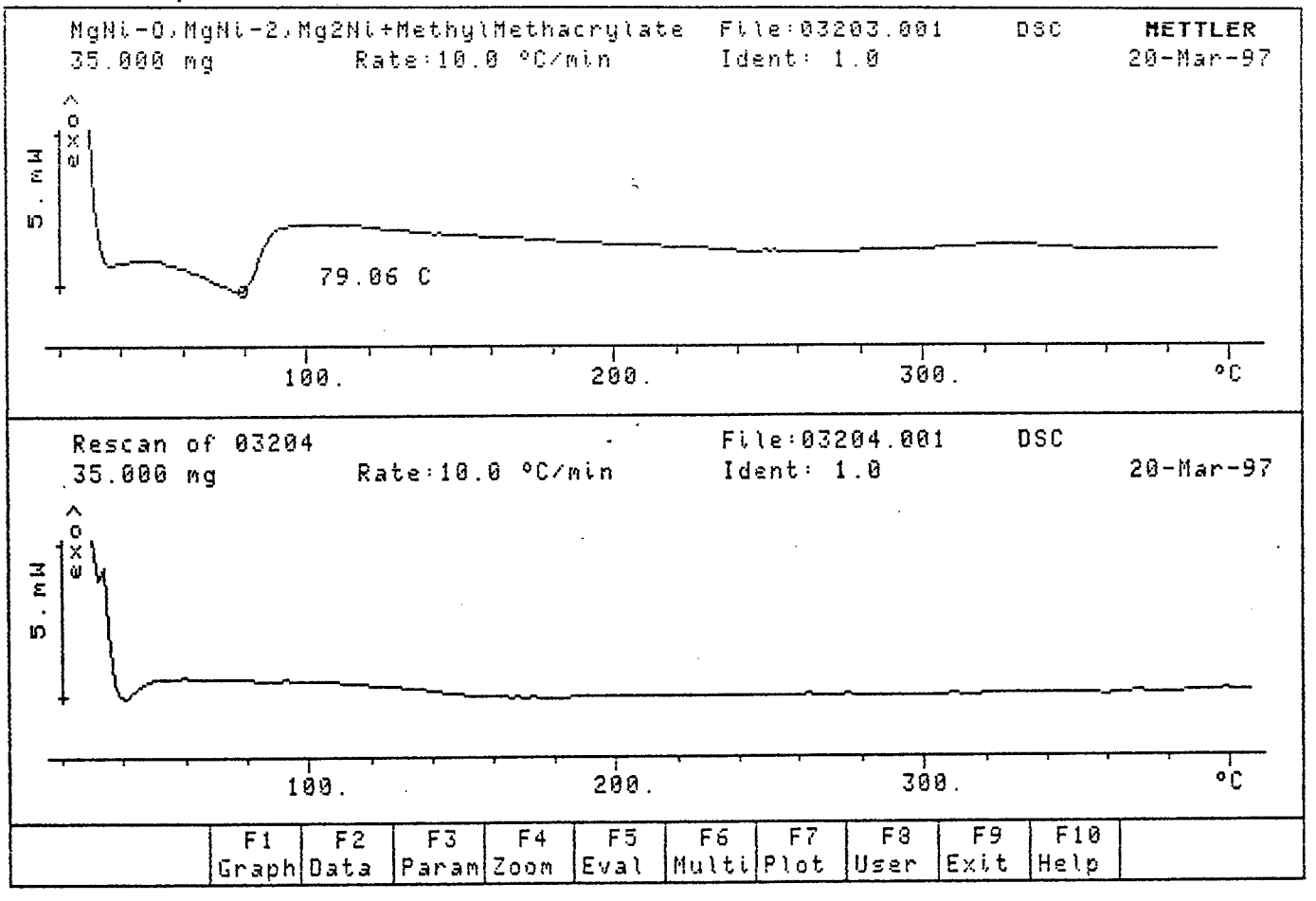


This document contains [redacted] and PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

MgNi-2

Mg2Ni & Methyl

Mehtacrylate

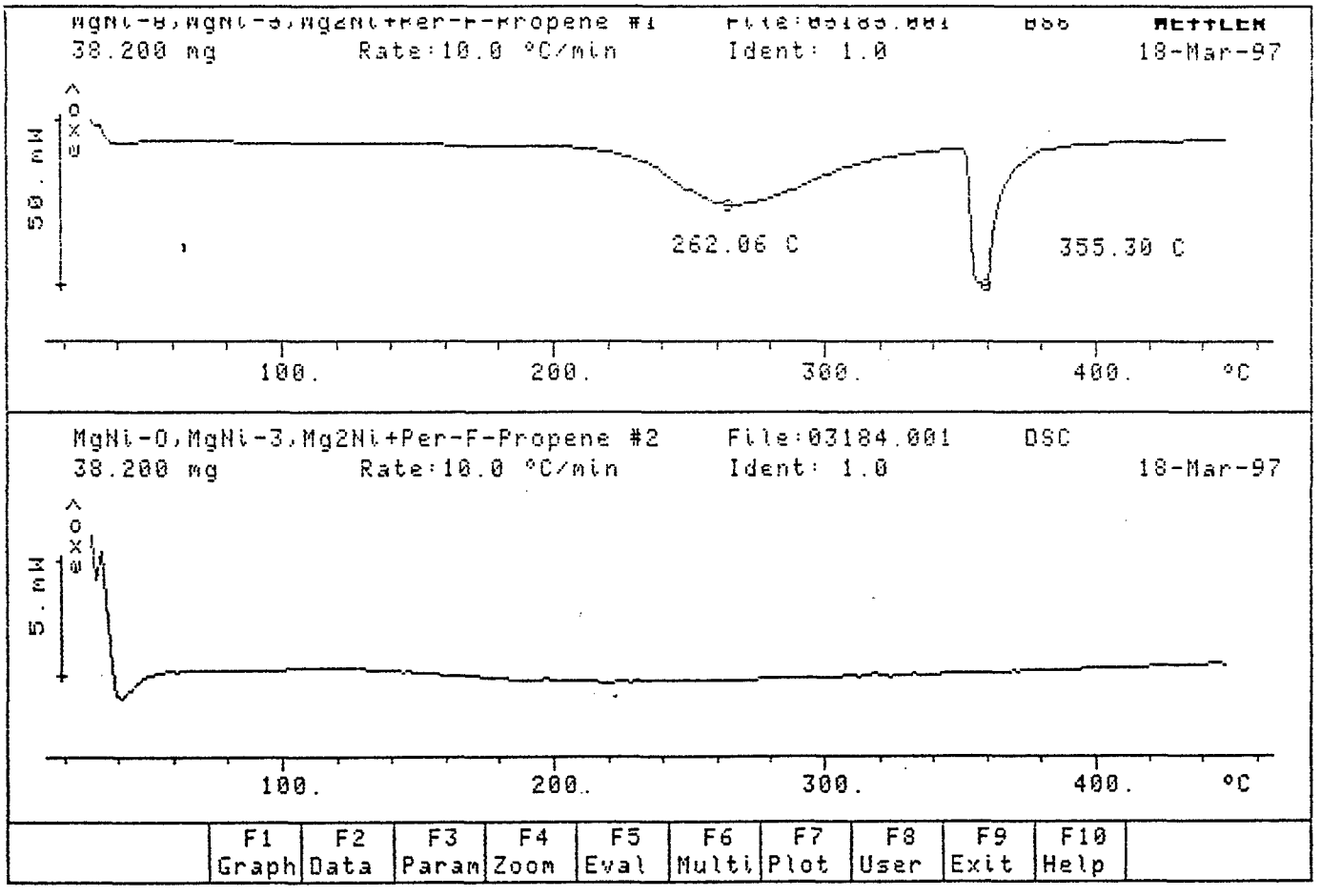


This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

MgNi-3

Mg2Ni &

Perfluoropropene

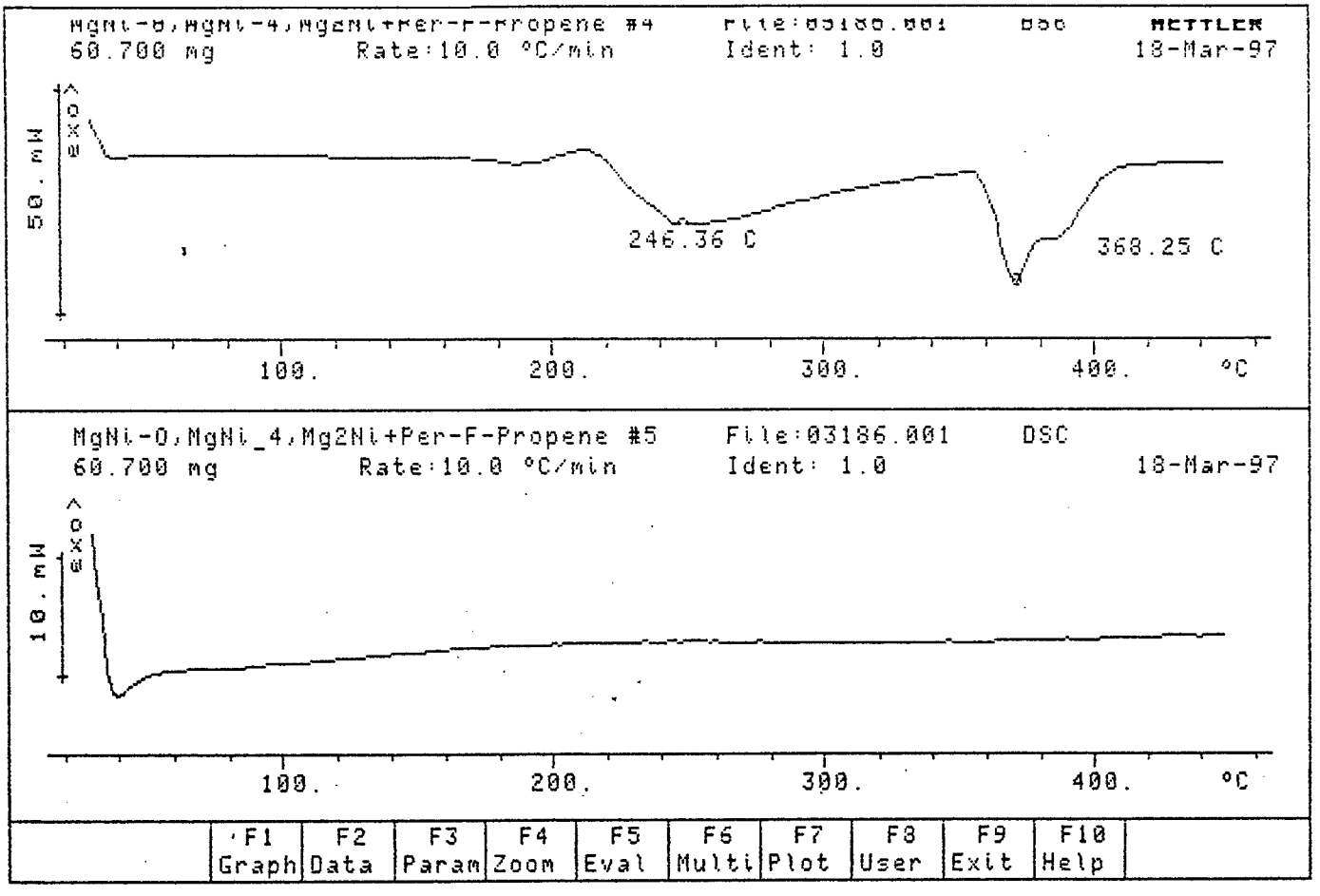


This document contains CONFIDENTIAL and PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

MgNi-4

Mg2Ni &

Perfluoropropene

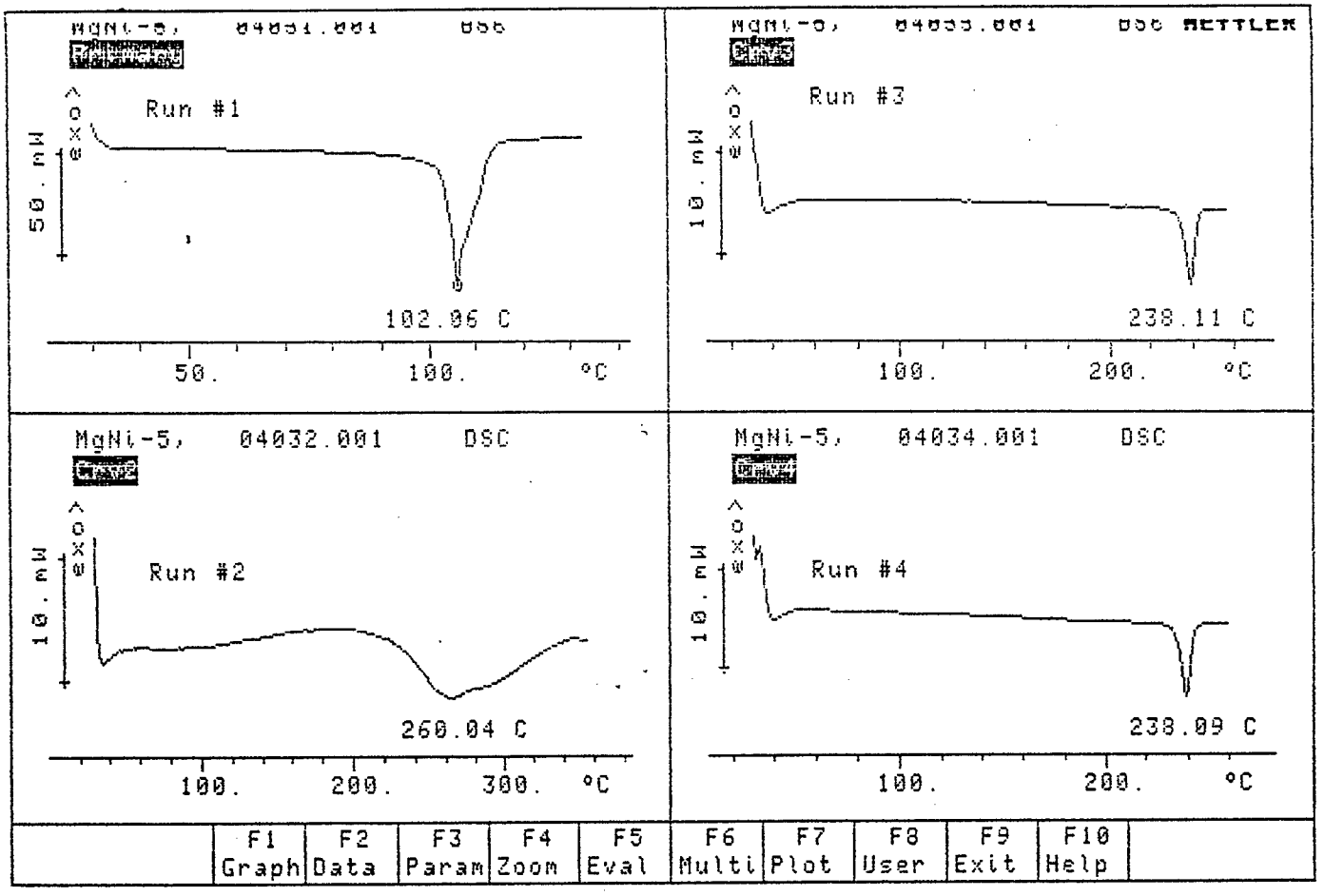


This document contains [redacted]PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

MgNi-5

Mg2Ni & Methyl

Methacrylate

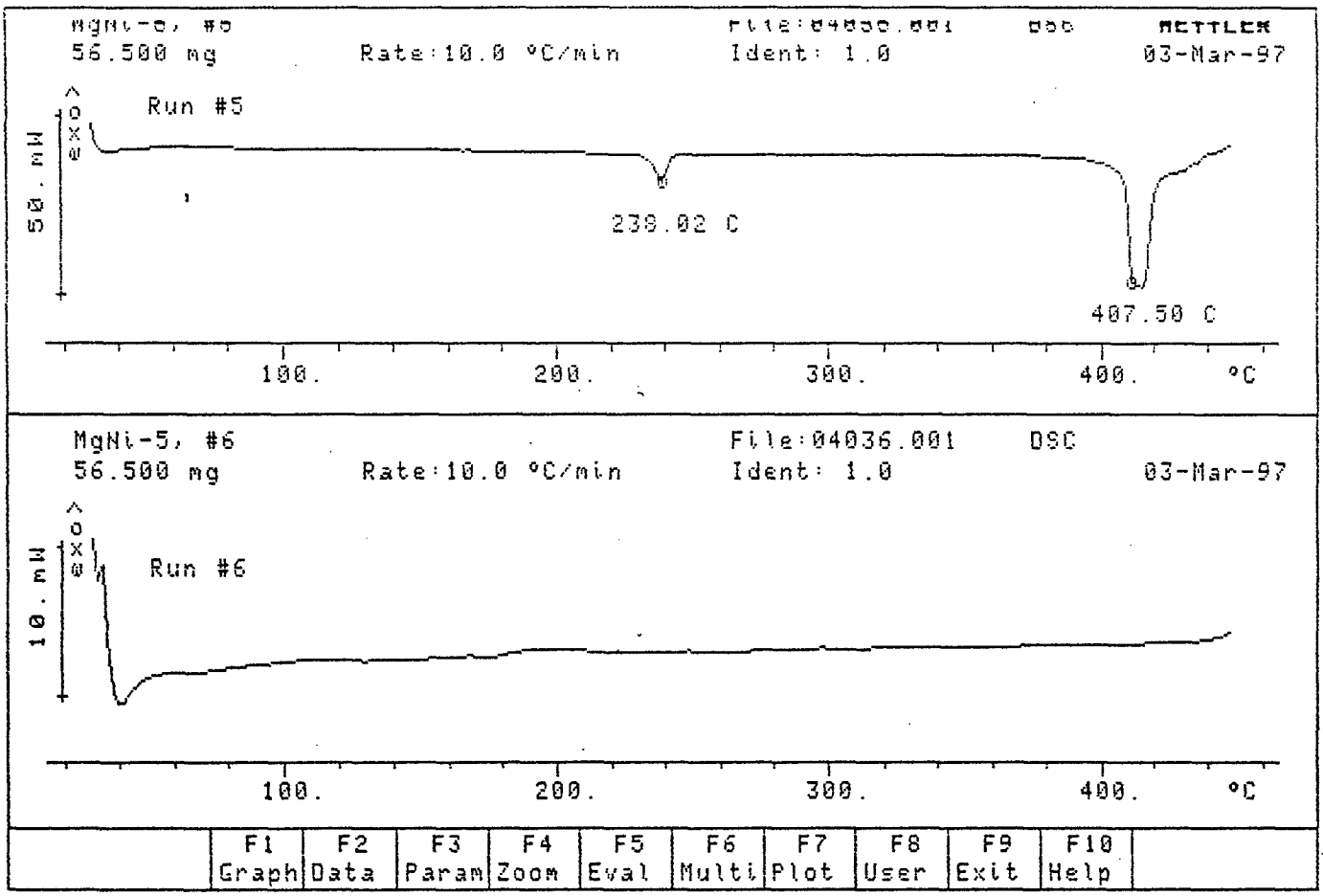


This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

MgNi-5

Mg2Ni & Methyl

Methacrylate

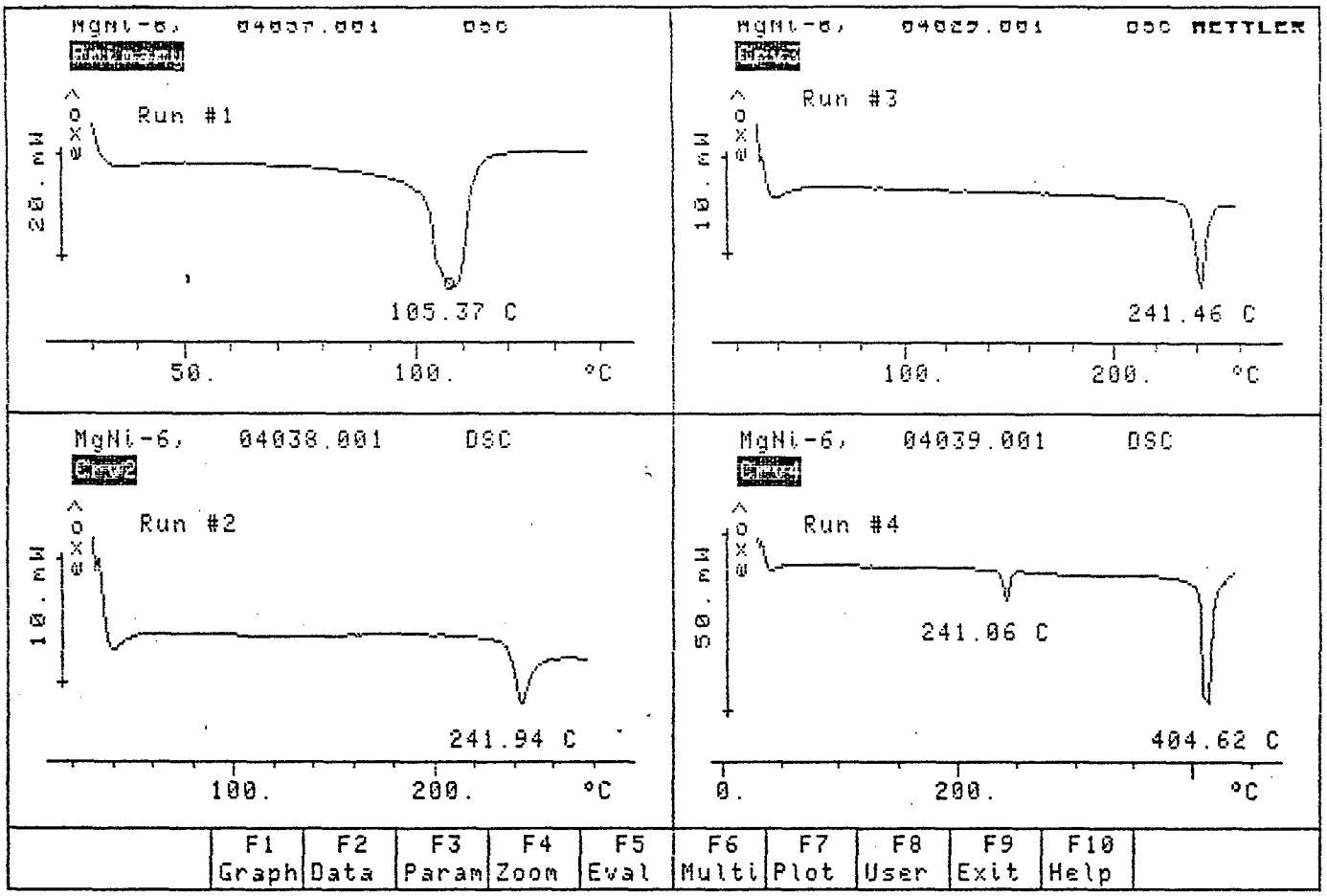


document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

MgNi-6

Mg2Ni & Methyl

Methacrylate

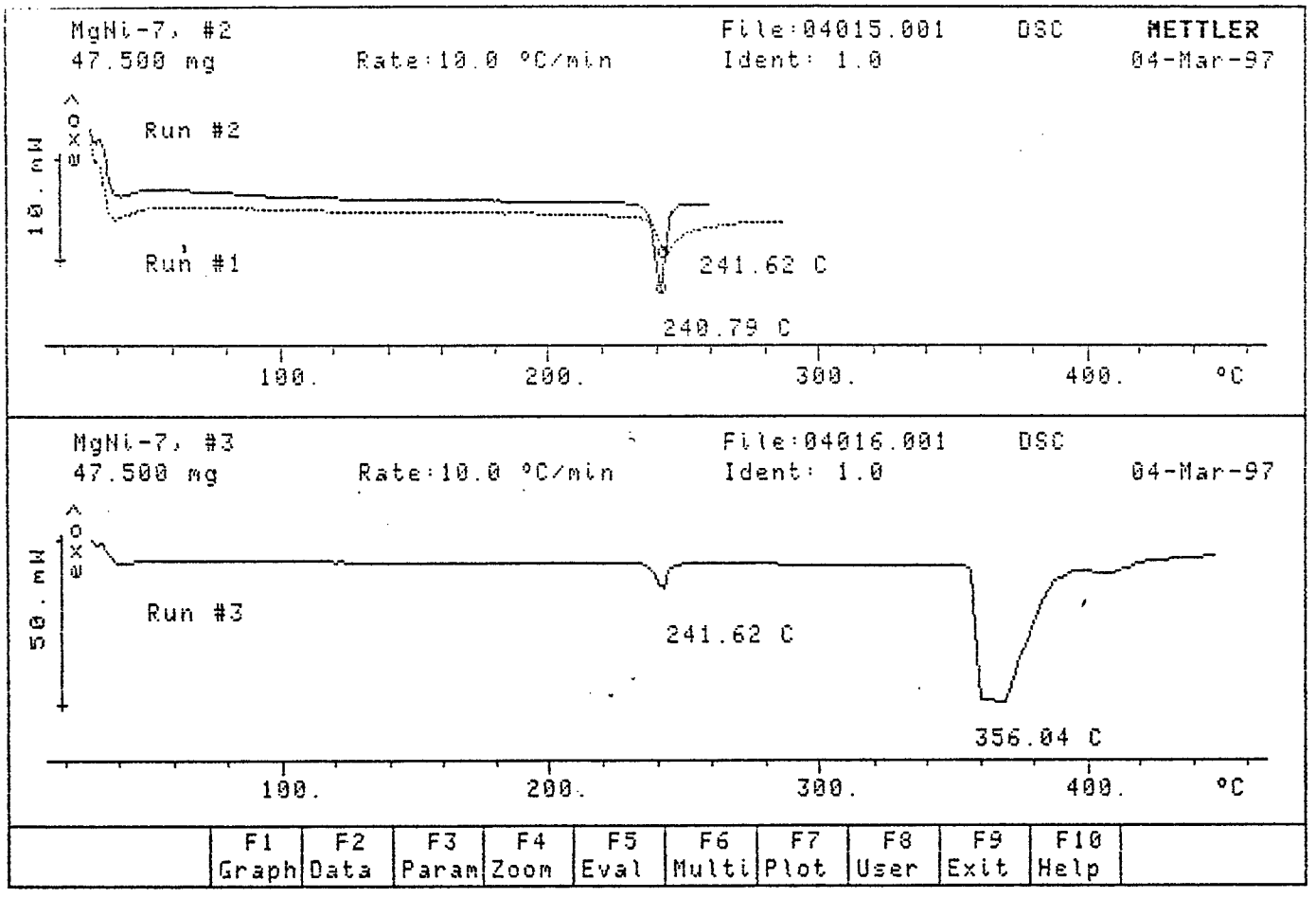


...ocument contains [redacted] PROPRIETARY ...rmation of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

MgNi-7

Mg2Ni &

Perfluoropropane

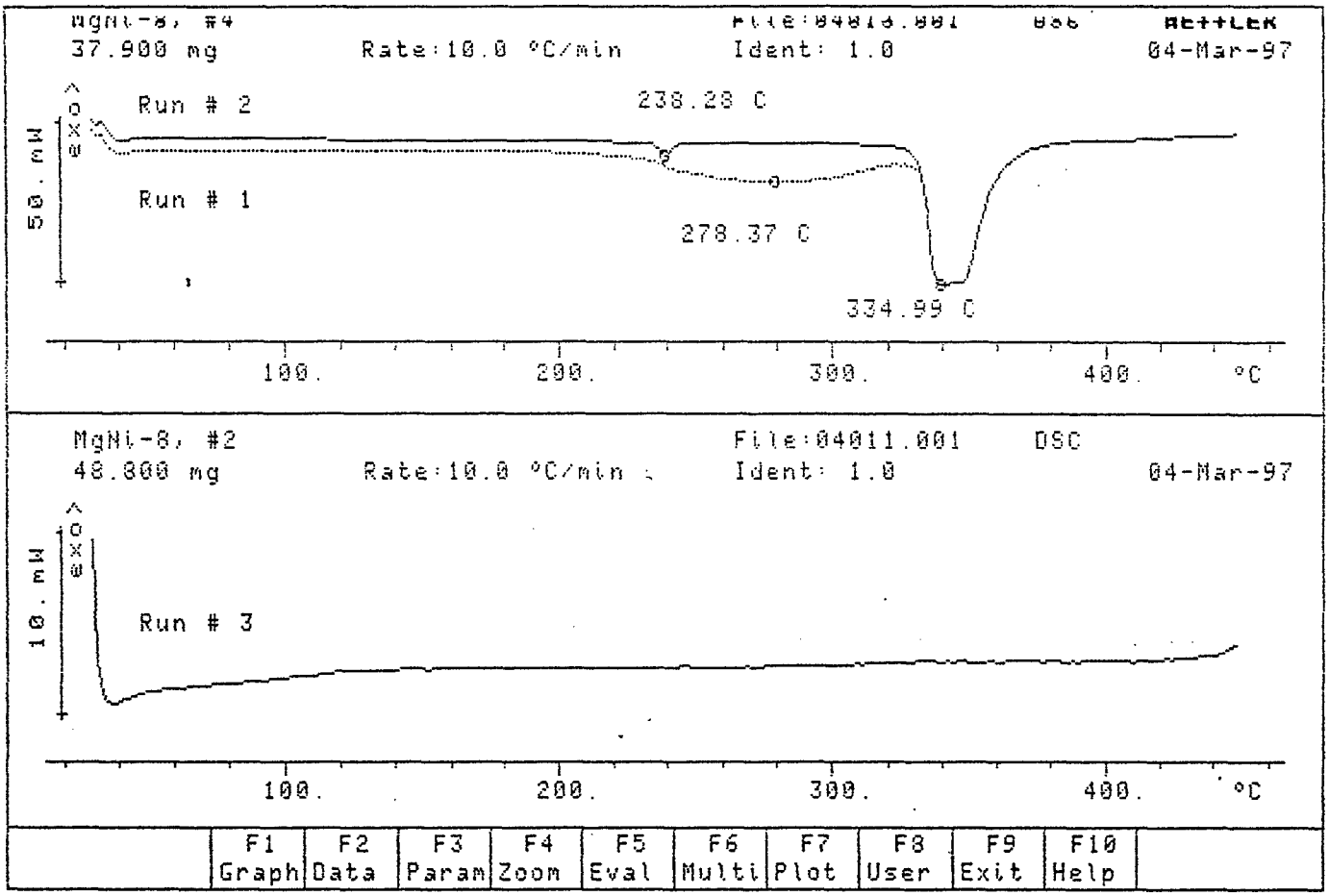


This document contains CONFIDENTIAL and PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

MgNi-8

Mg2Ni &

Perfluoropropene

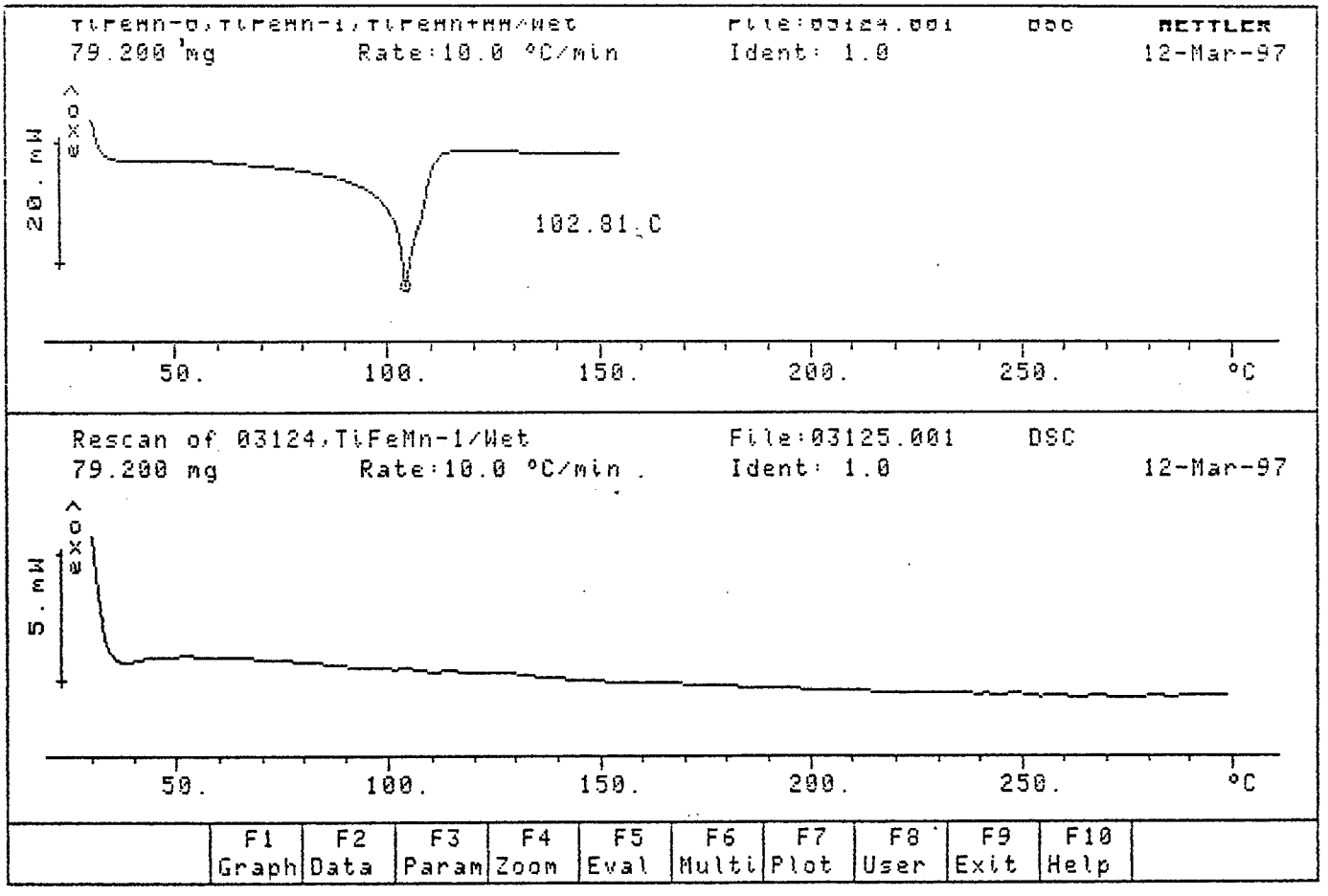


This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

TiFeMn-1

TiFeMn & Methyl

Methacrylate

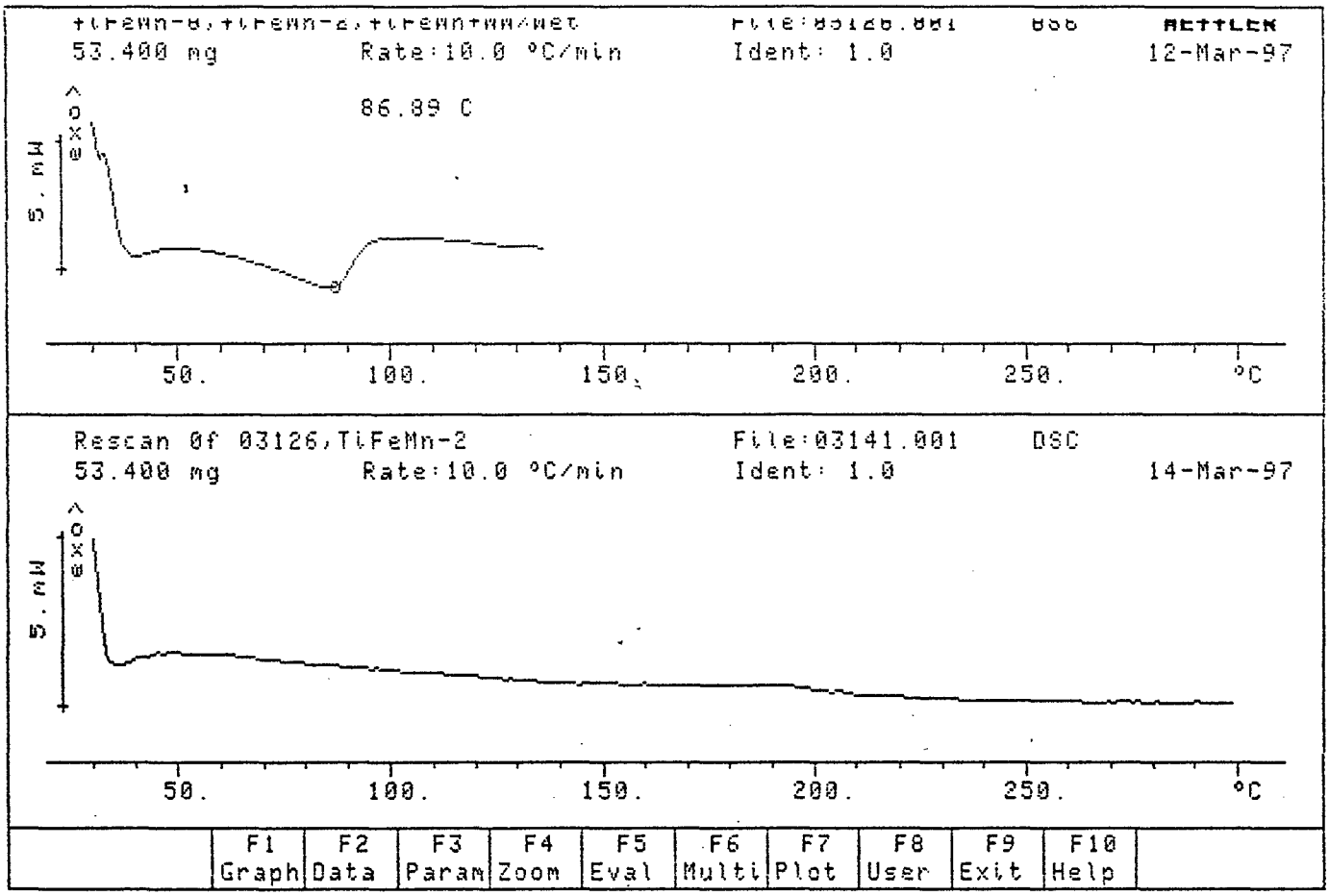


s document contains [redacted]PROPRIETARY
ormation of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

TiFeMn-2

TiFeMn & Methyl

Methacrylate

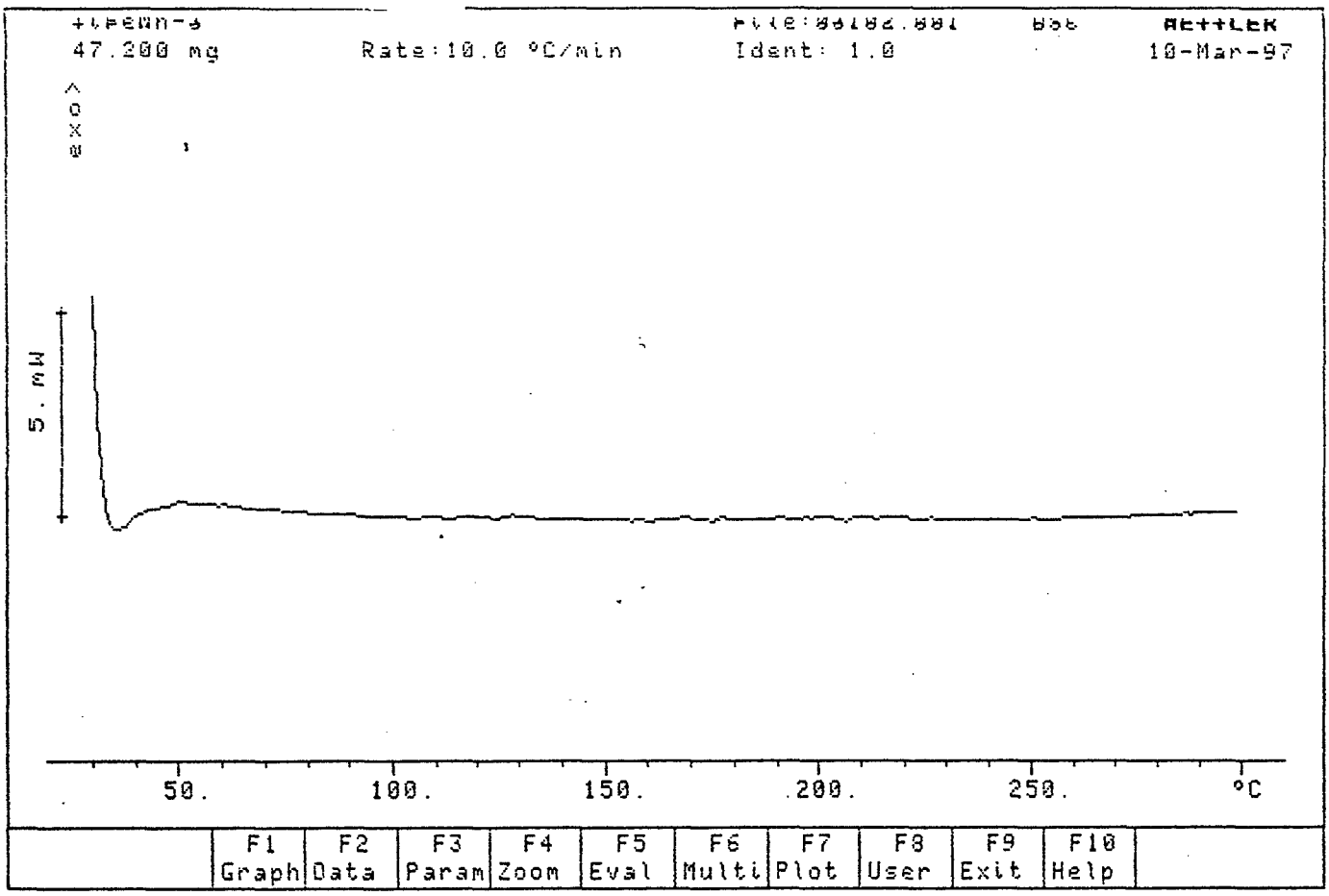


This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

TiFeMn-3

TiFeMn &

Perfluoropropene

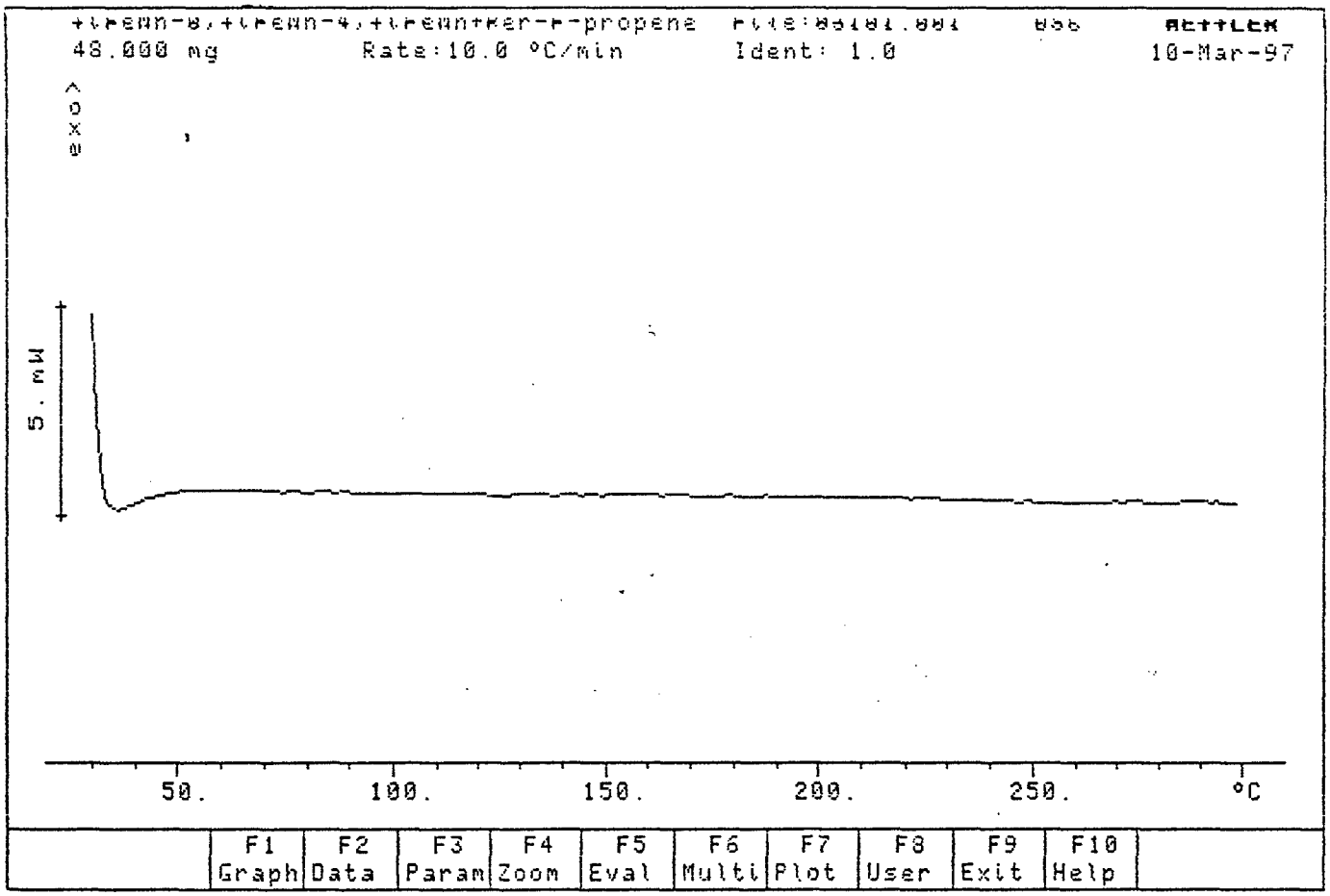


This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

TiFeMn-4

TiFeMn &

Perfluoropropene

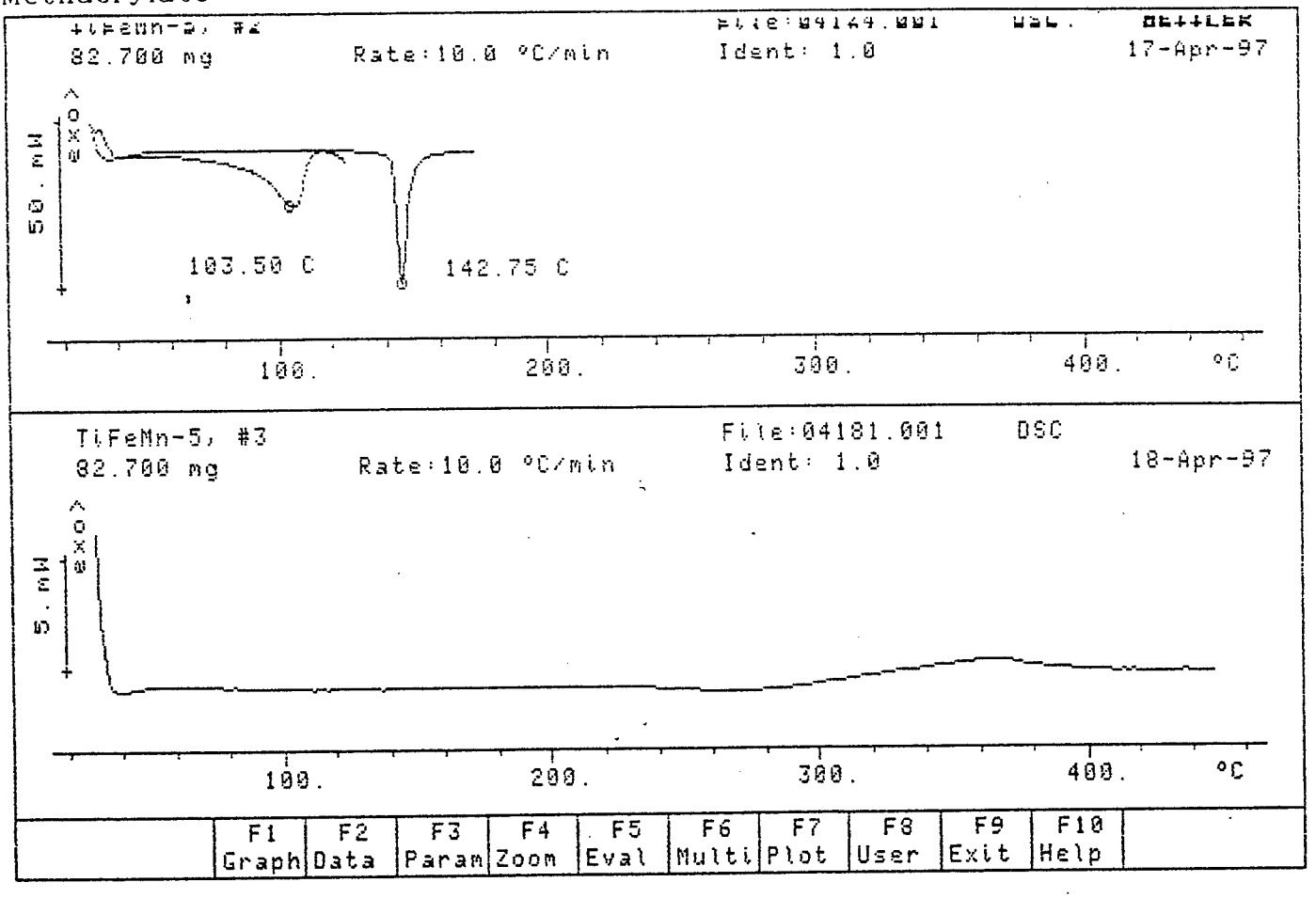


This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

TiFeMn-5

TiFeMn & Methyl

Methacrylate

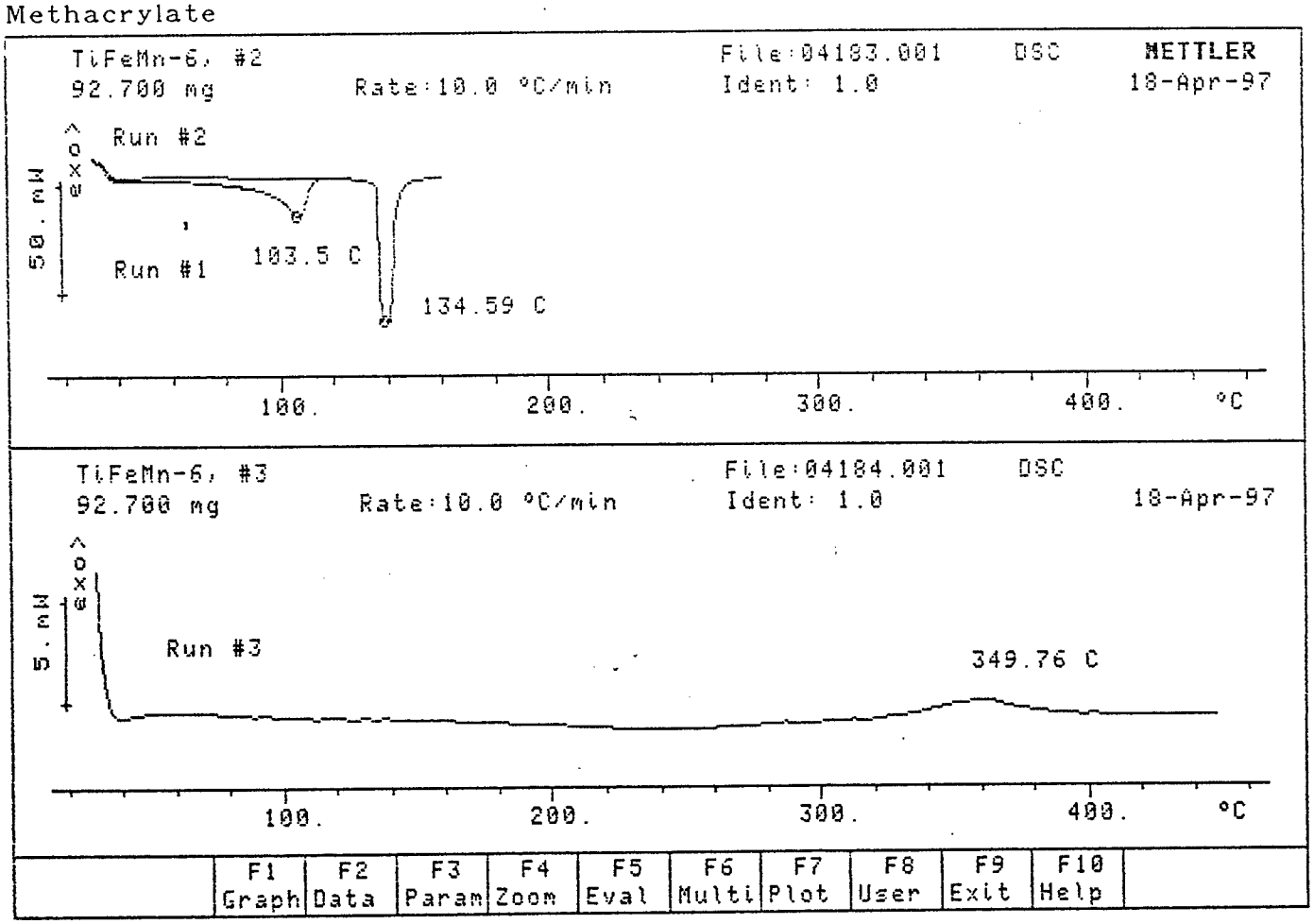


This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

TiFeMn-6

TiFeMn & Methyl

Methacrylate

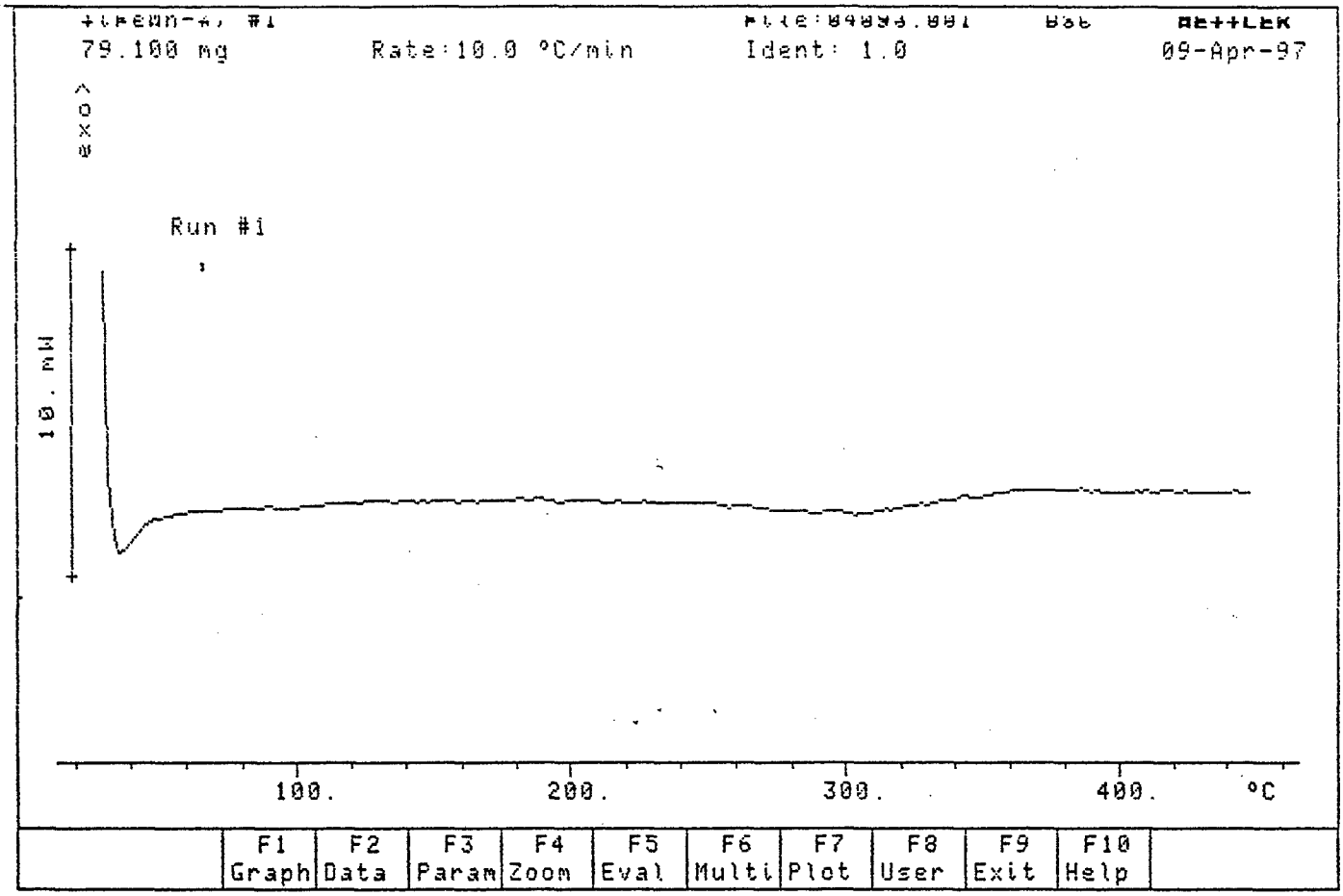


This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

TiFeMn-7

TiFeMn &

Perfluoropropene

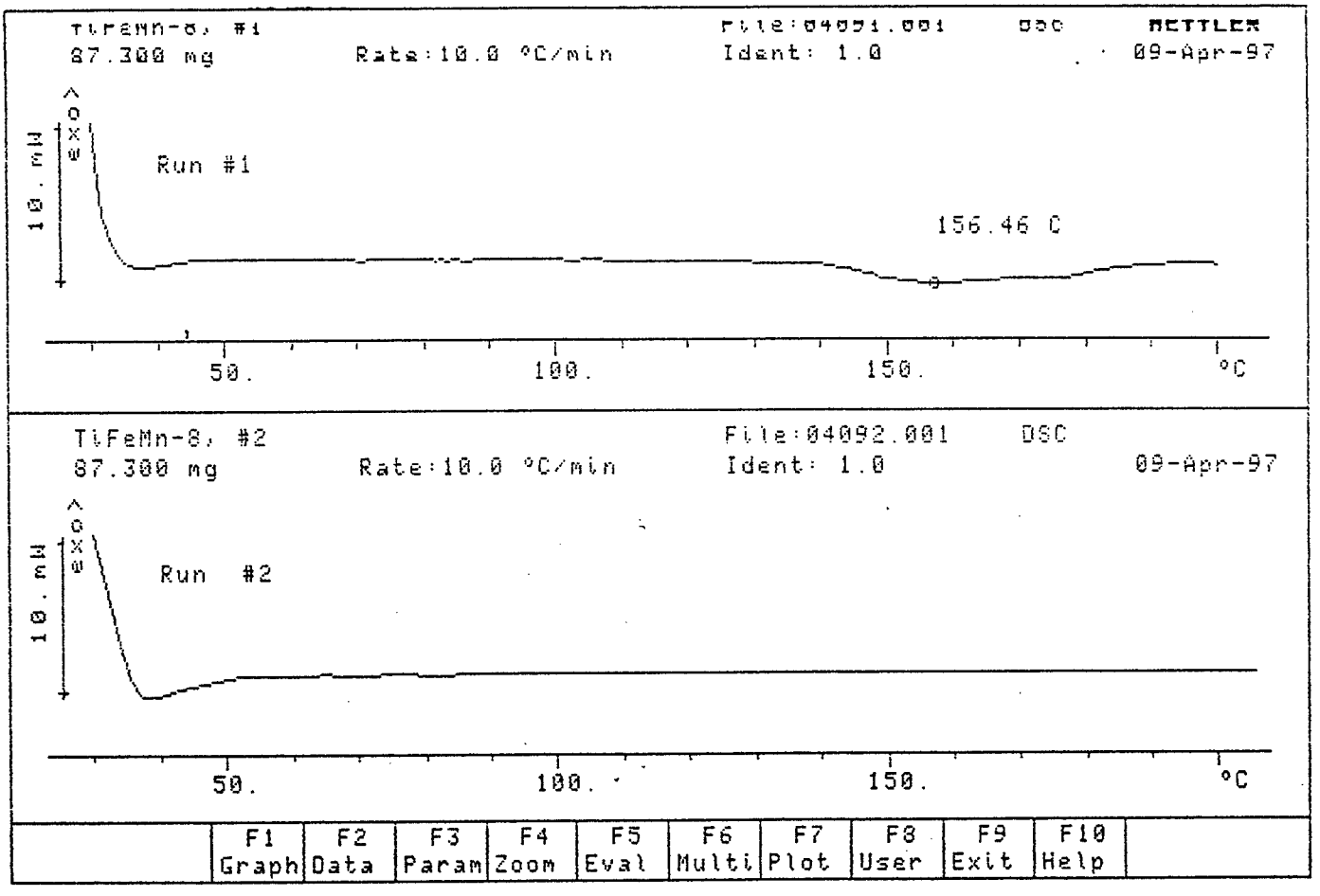


document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

TiFeMn-8

TiFeMn &

Perfluoropropene

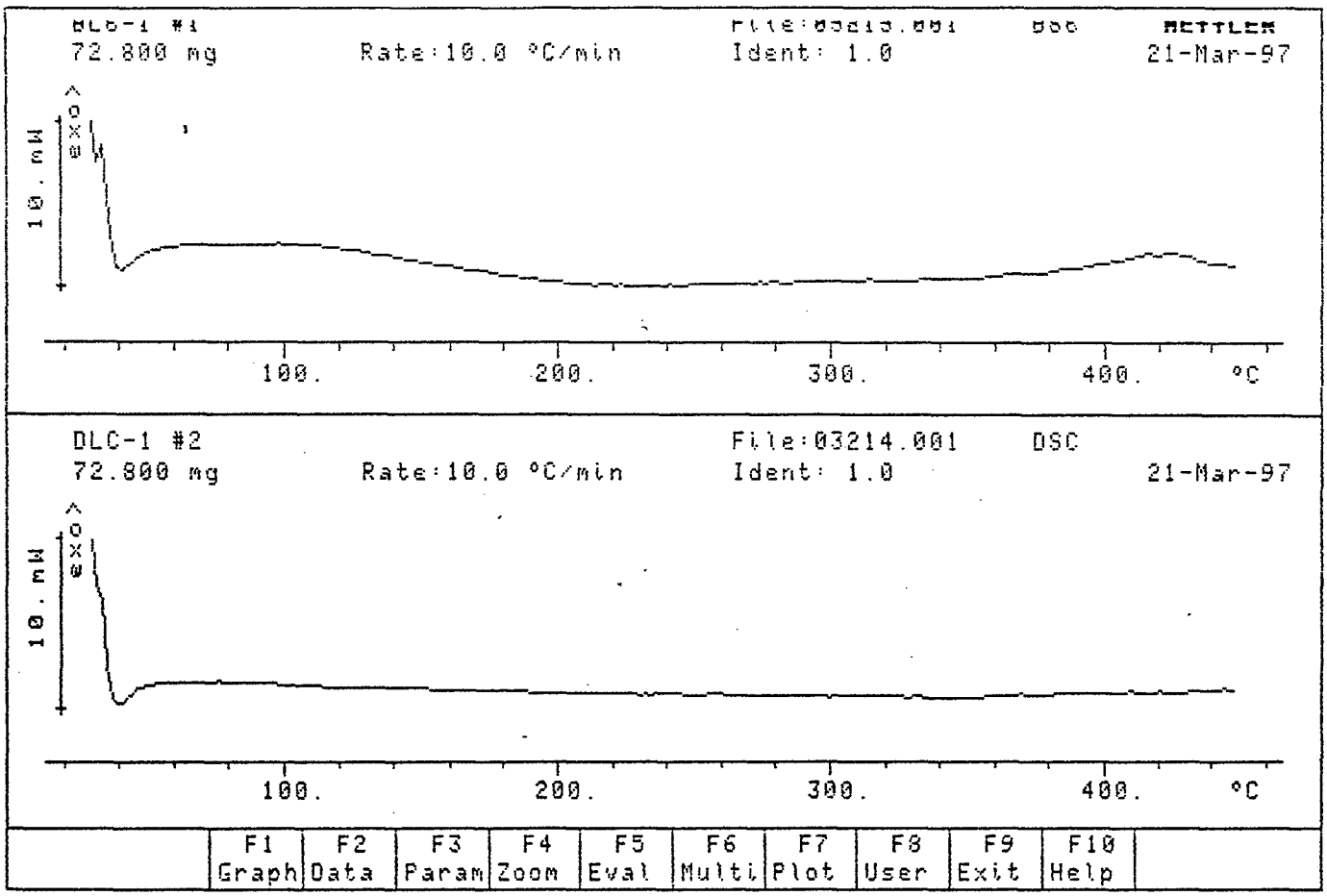


This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

DLC-1

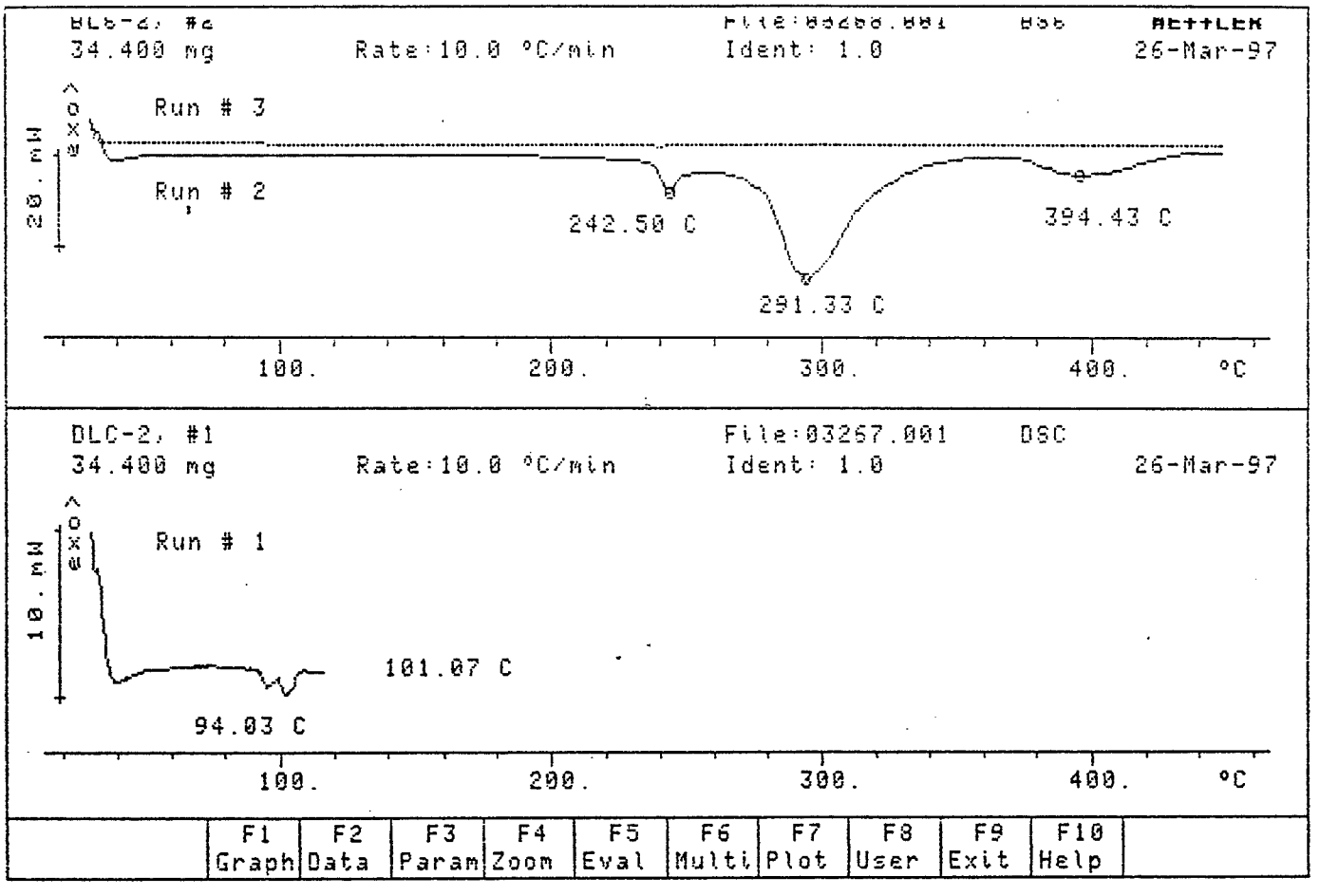
CaNi5 - Oxide

Poly(Dimethylsiloxane)



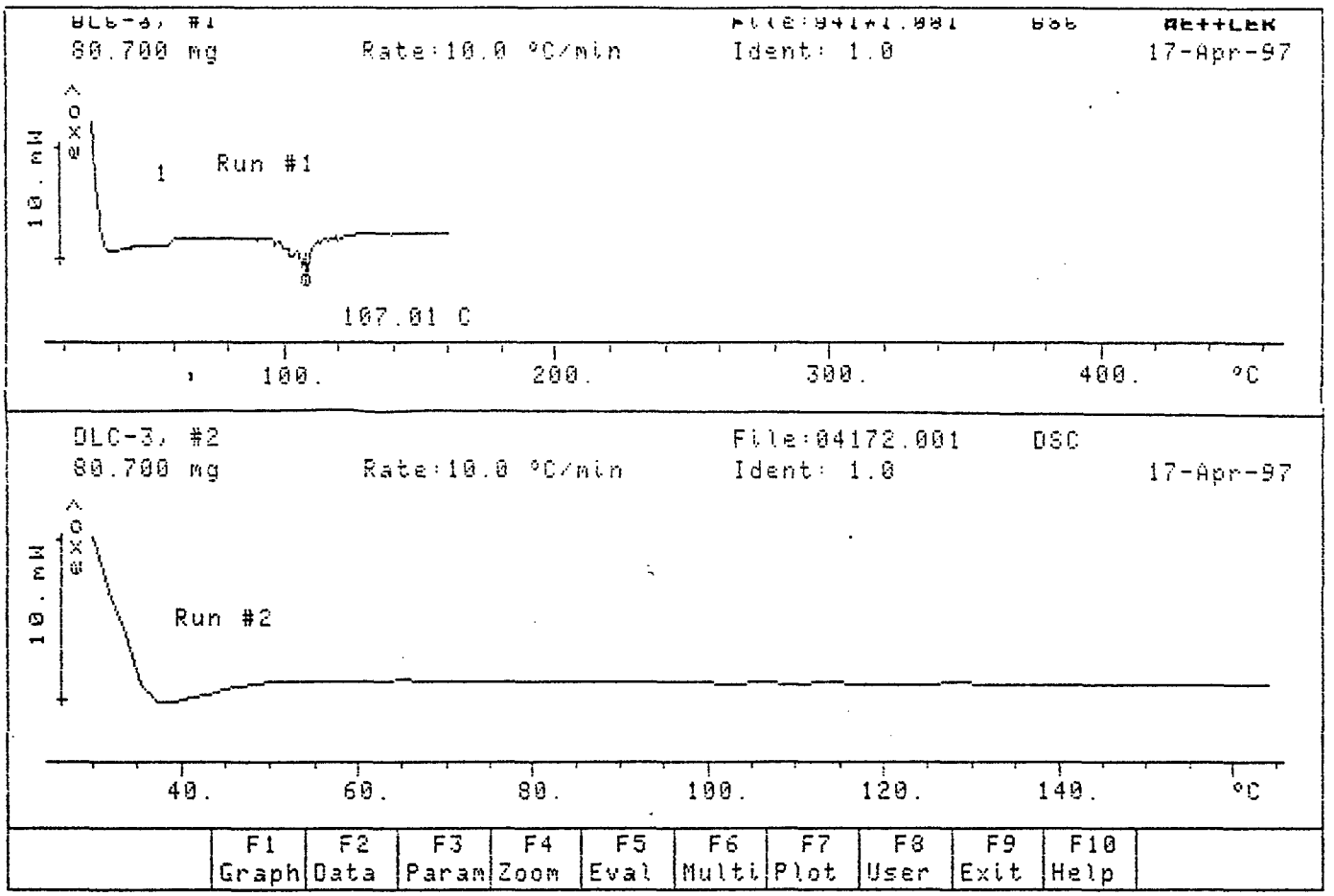
This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

DLC-2
Mg2Ni-Hydride
Poly(dimethylsiloxane)
5% H2O



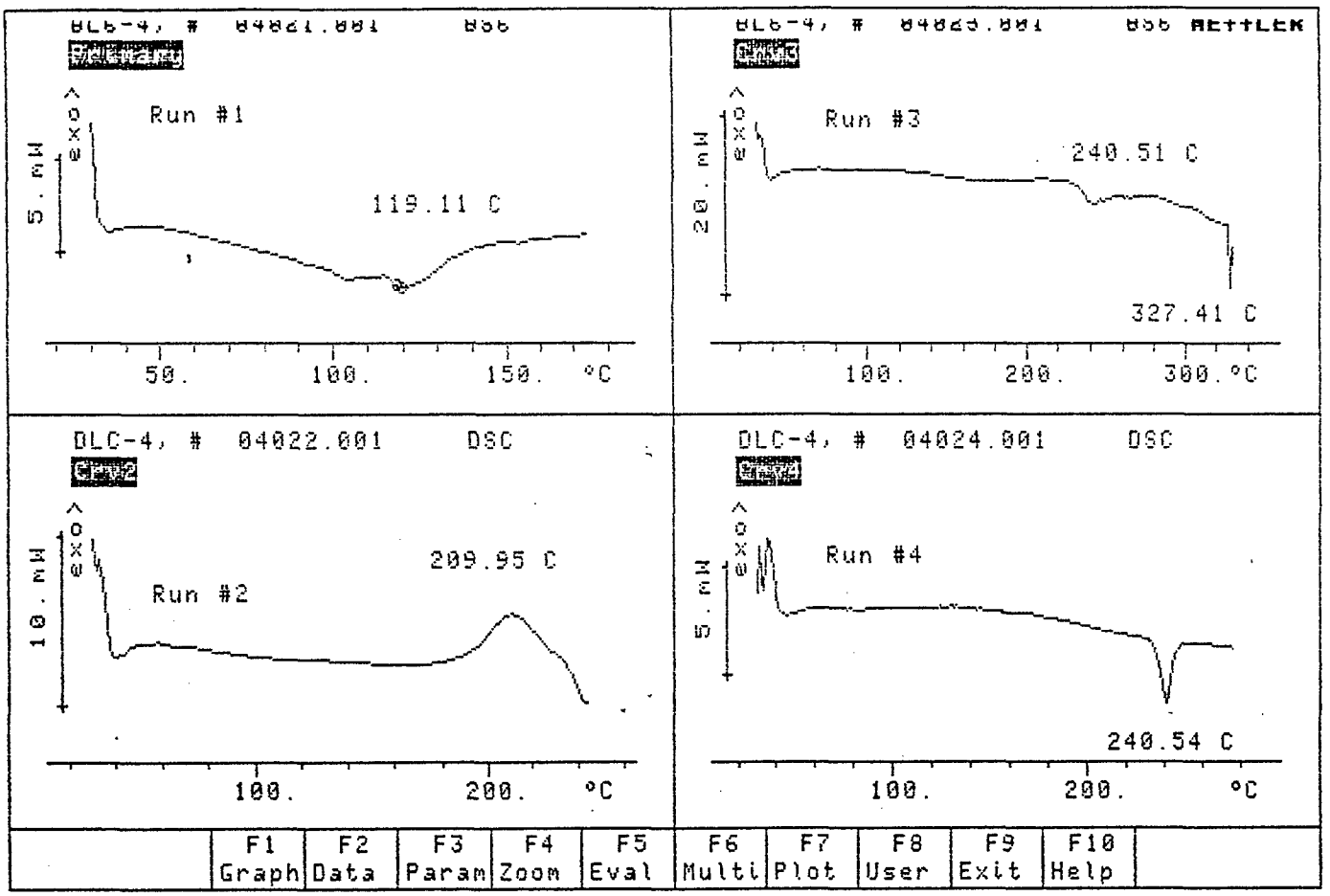
This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

DLC-3
TiFeMn-Oxide
Poly(dimethylsiloxane)
& 5% H2O



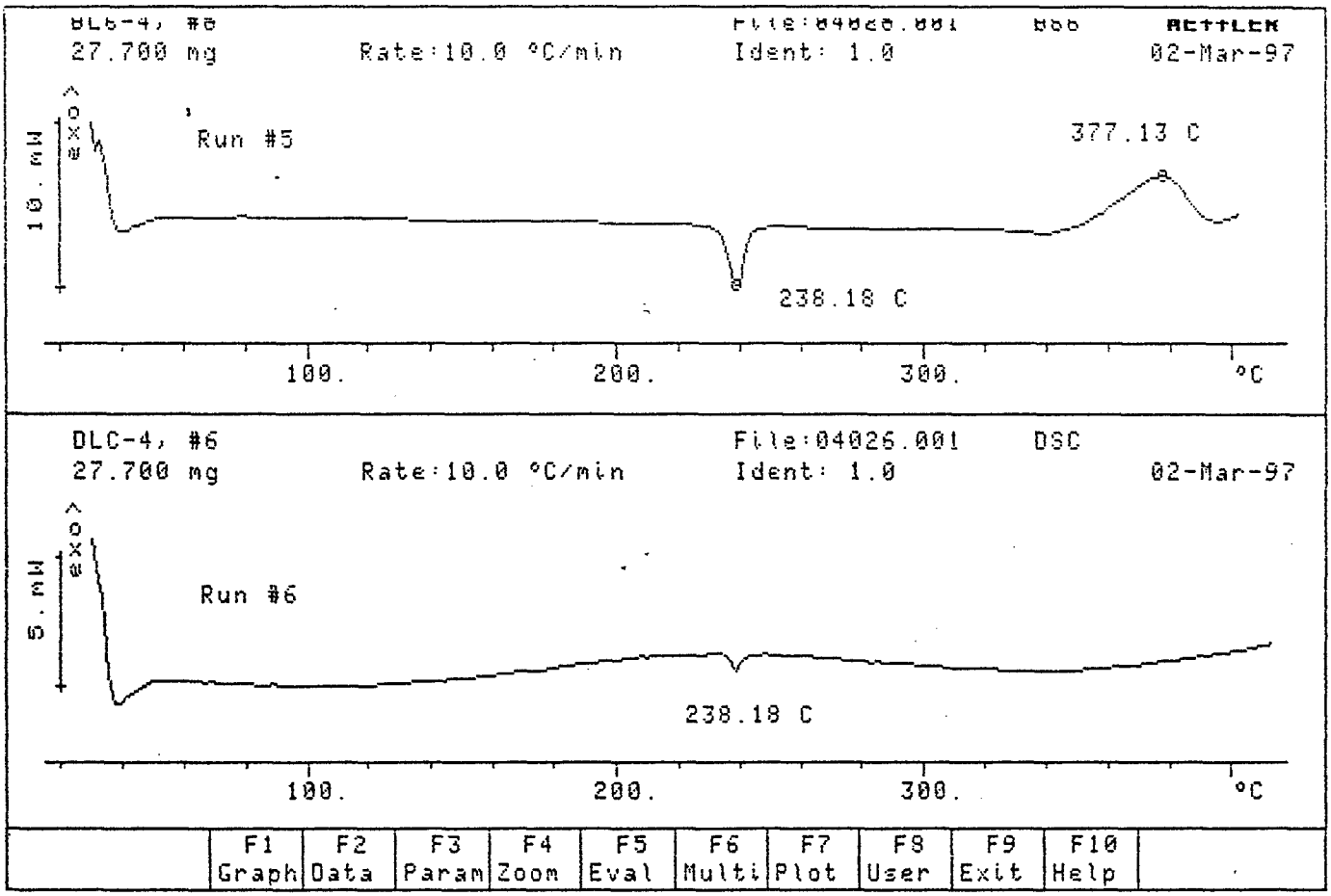
This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

DLC-4
Mg2Ni-Hydride
Poly(ethylene glycol)
5% H2O



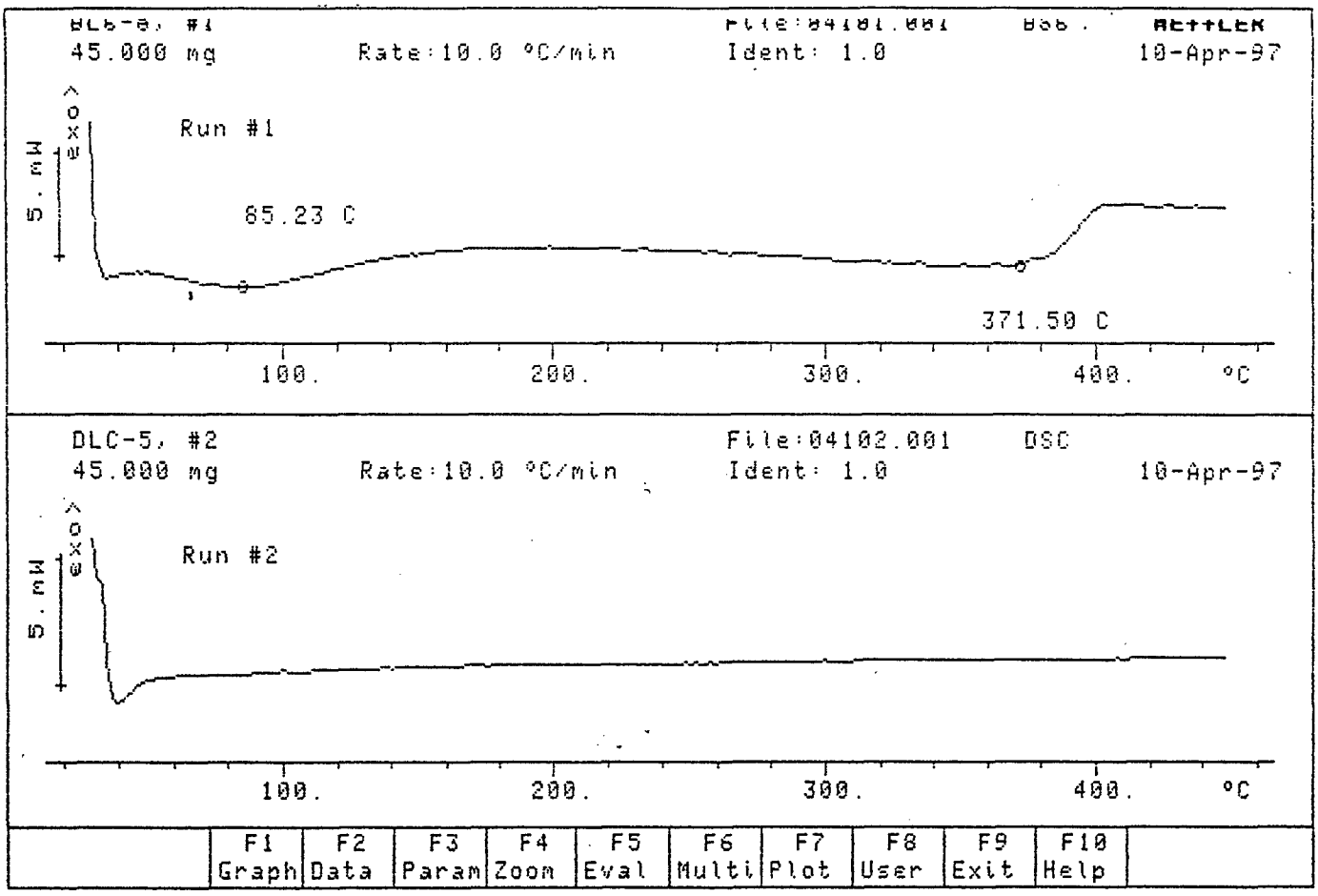
This document contains CONFIDENTIAL and PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

DLC-4
Mg2Ni-Hydride
Poly(ethylene glycol)
5% H2O



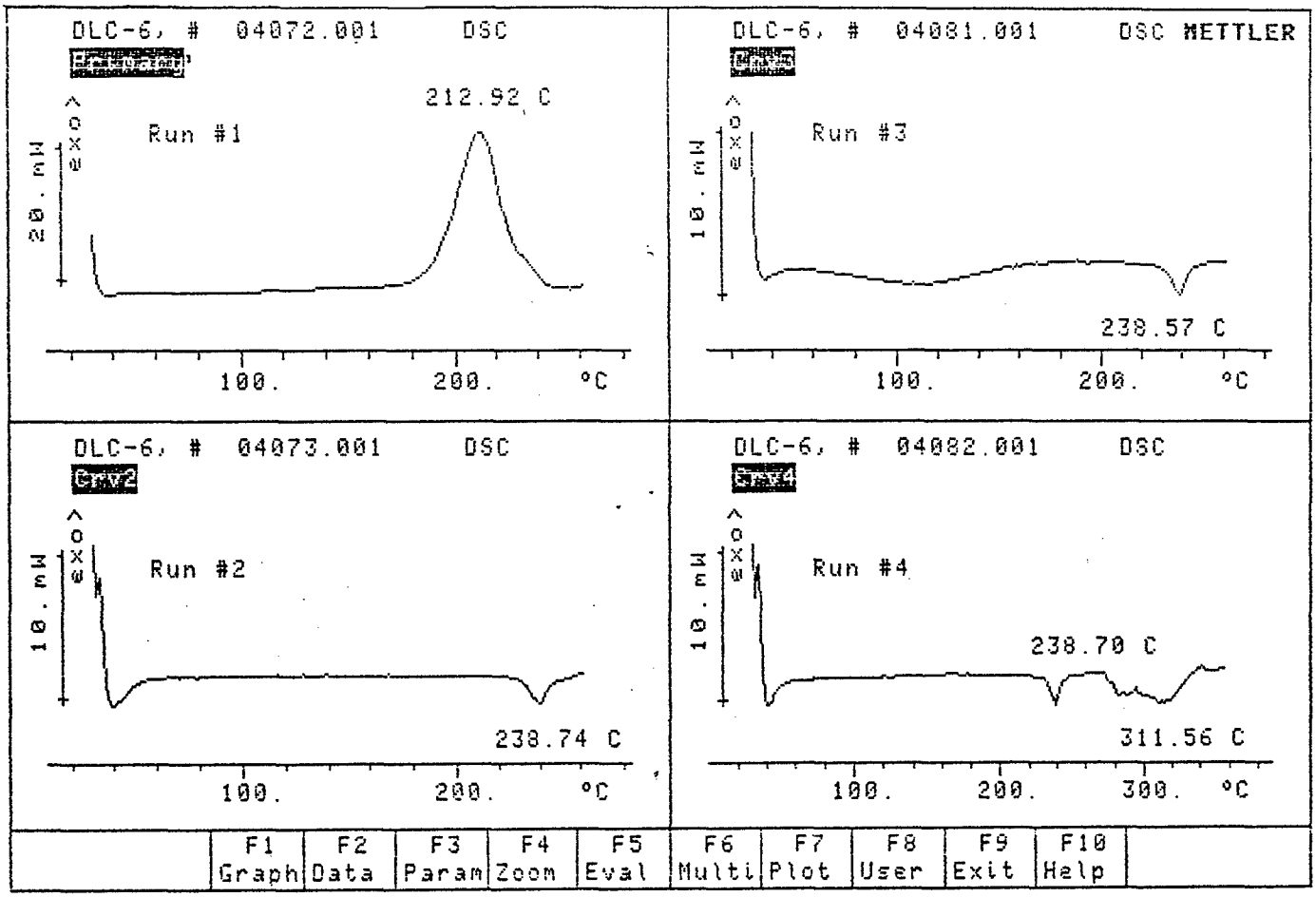
This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

DLC-5
TiFeMn-Oxide
Poly(ethylene glycol)
5% H2O



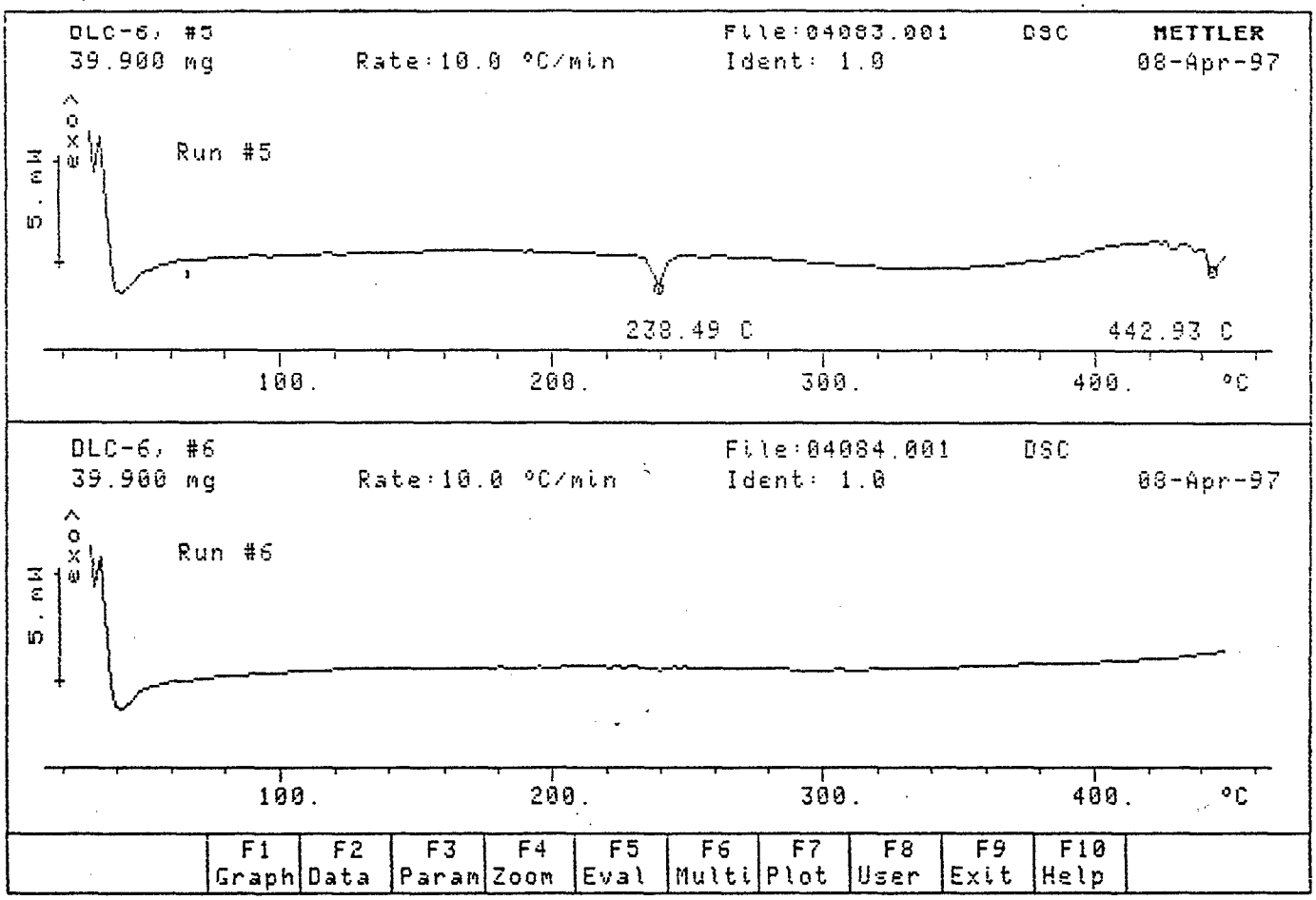
This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

DLC-6
Mg2Ni-Hydride
Poly(ethylene glycol)
methyl ether



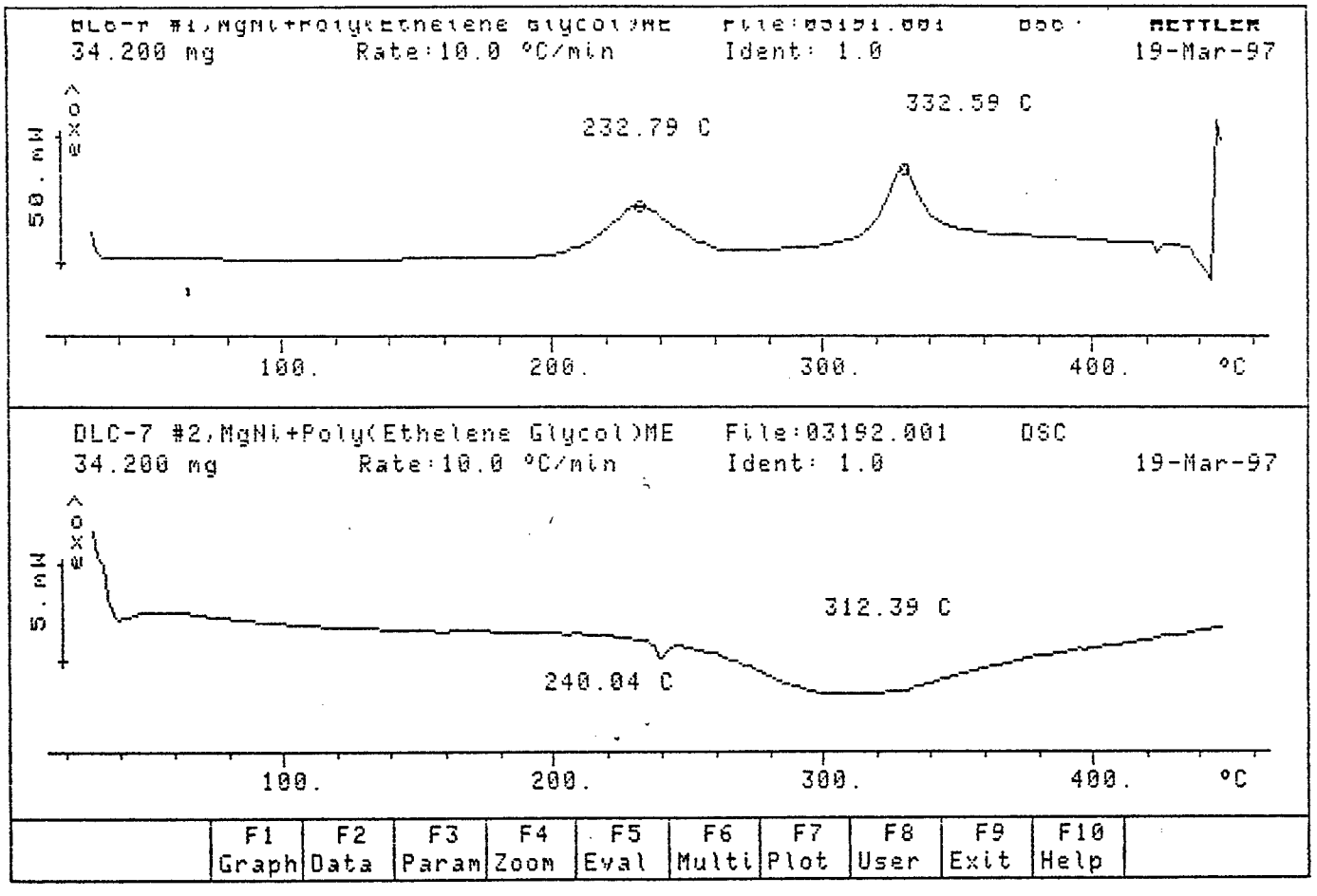
This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

DLC-6
Mg2Ni-Hydride
Poly(ethylene glycol)
methyl ether



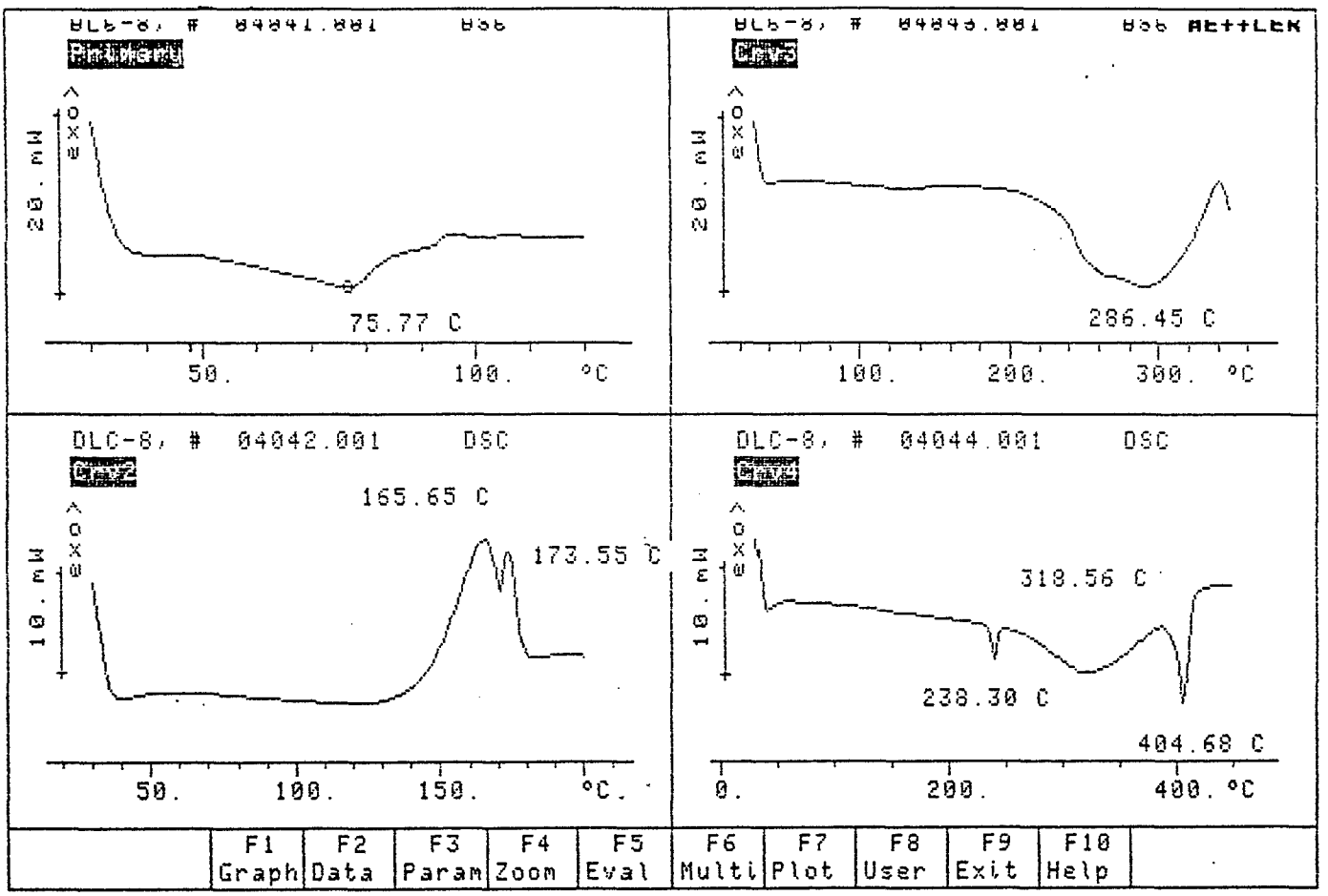
This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

DLC-7
Mg2Ni & Poly
(Ethelene Glycol)
Methyl Ether



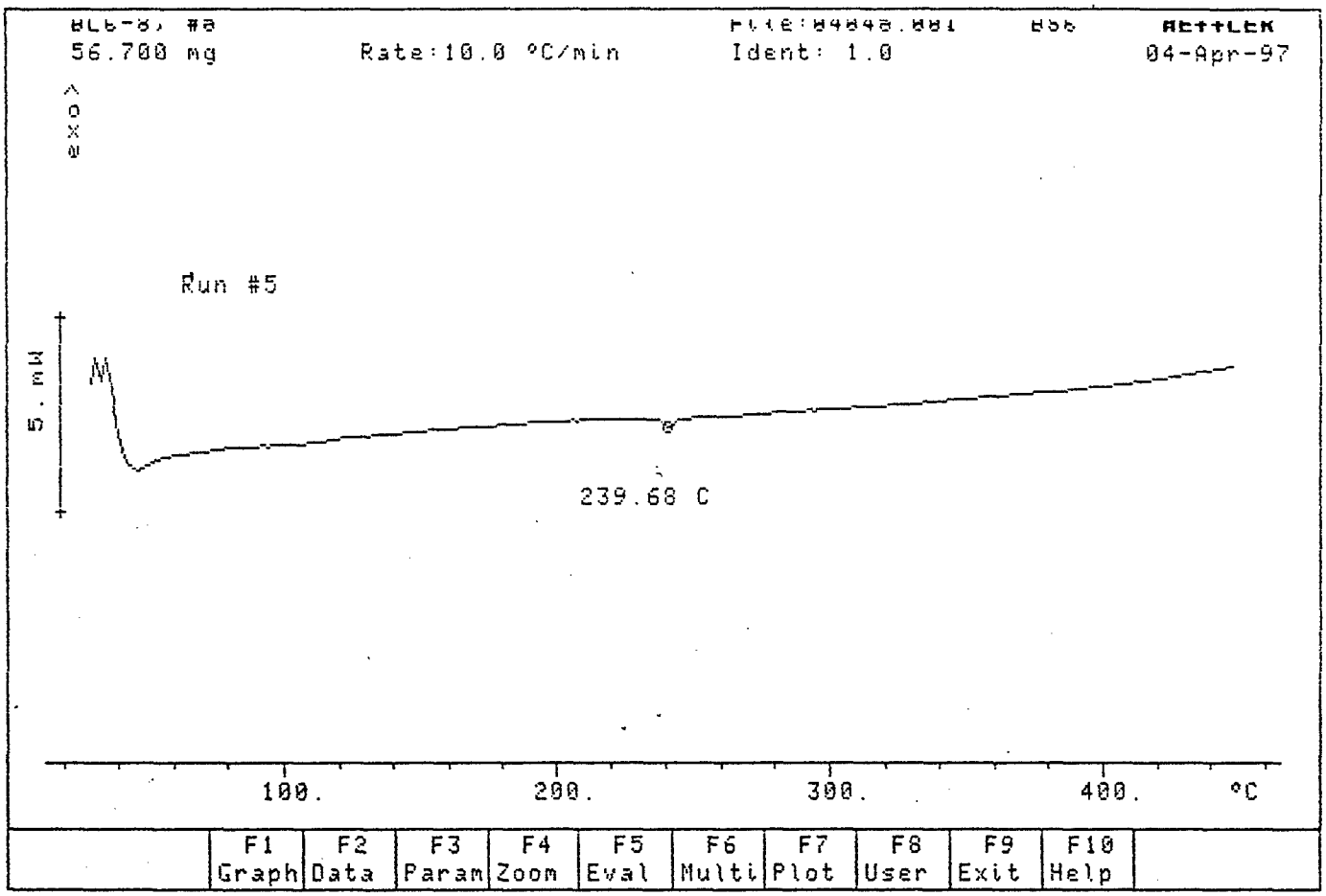
This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

DLC-8
Mg2Ni-Hydride
Propylene glycol
butyl ether



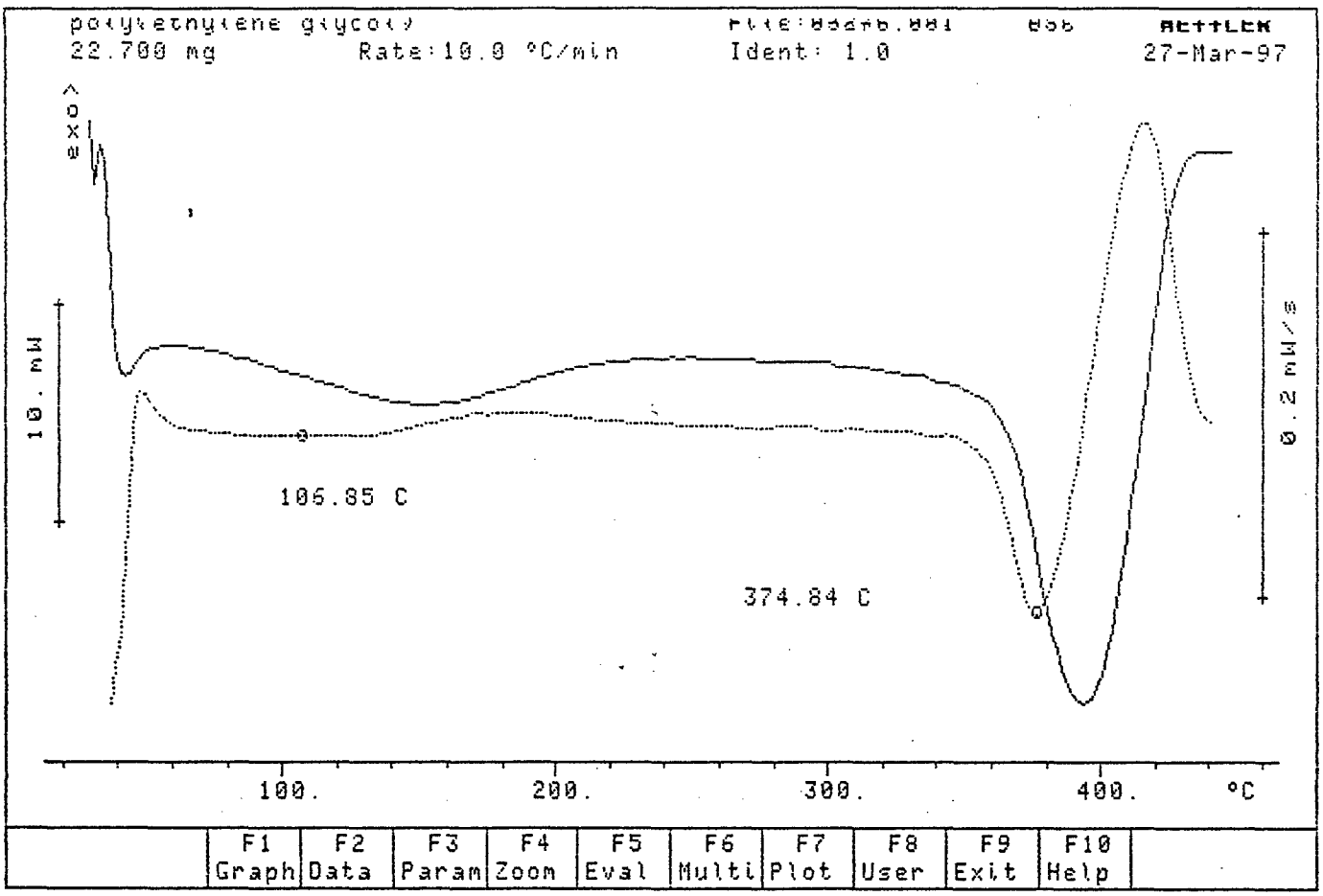
This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

DLC-8
Mg2Ni-Hydride
Propolene glycol
butyl ether



This document contains CONFIDENTIAL and PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

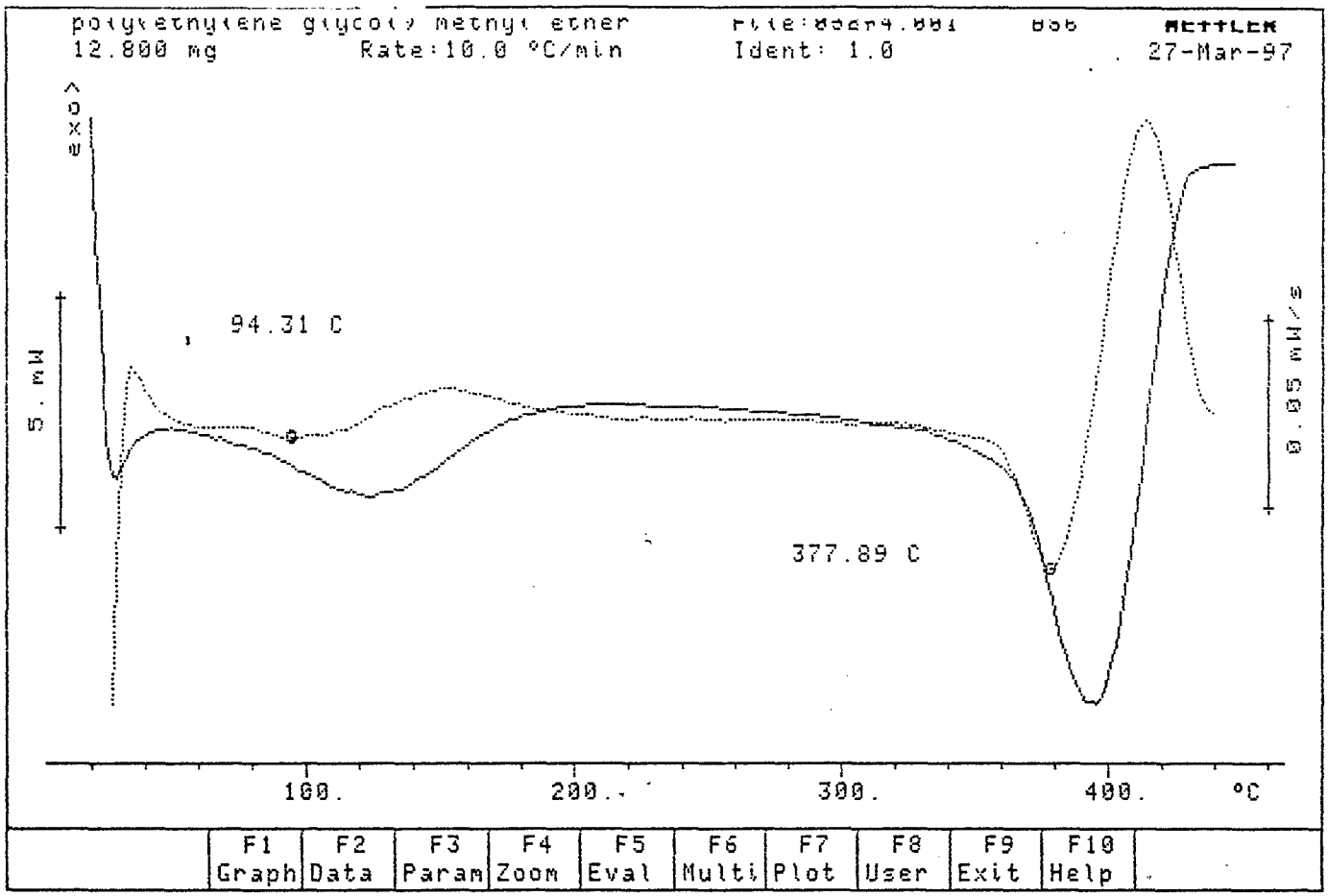
Poly(ethylene glycol)



This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

Poly(ethylene glycol)

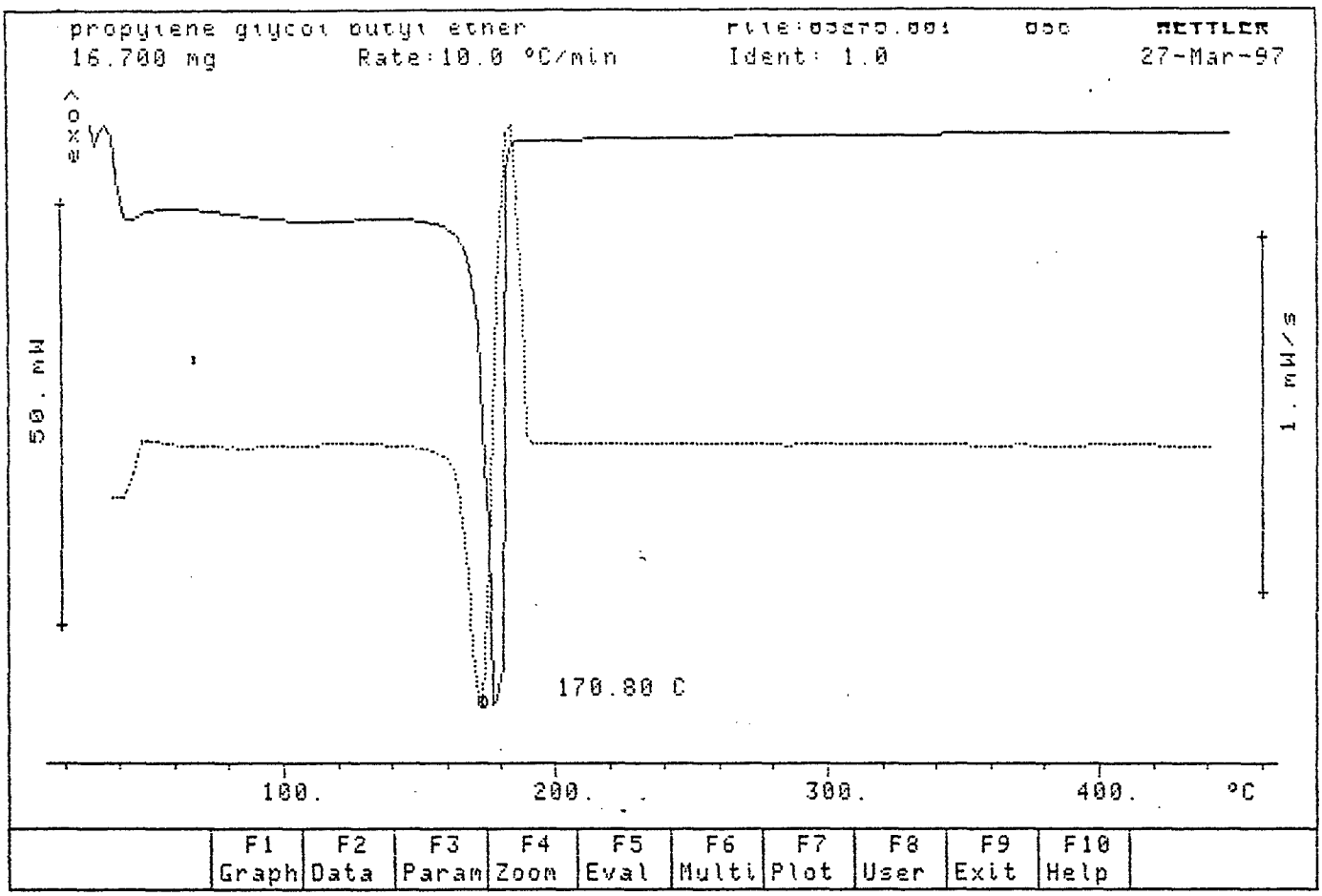
methyl ether



This document contains [redacted] and PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

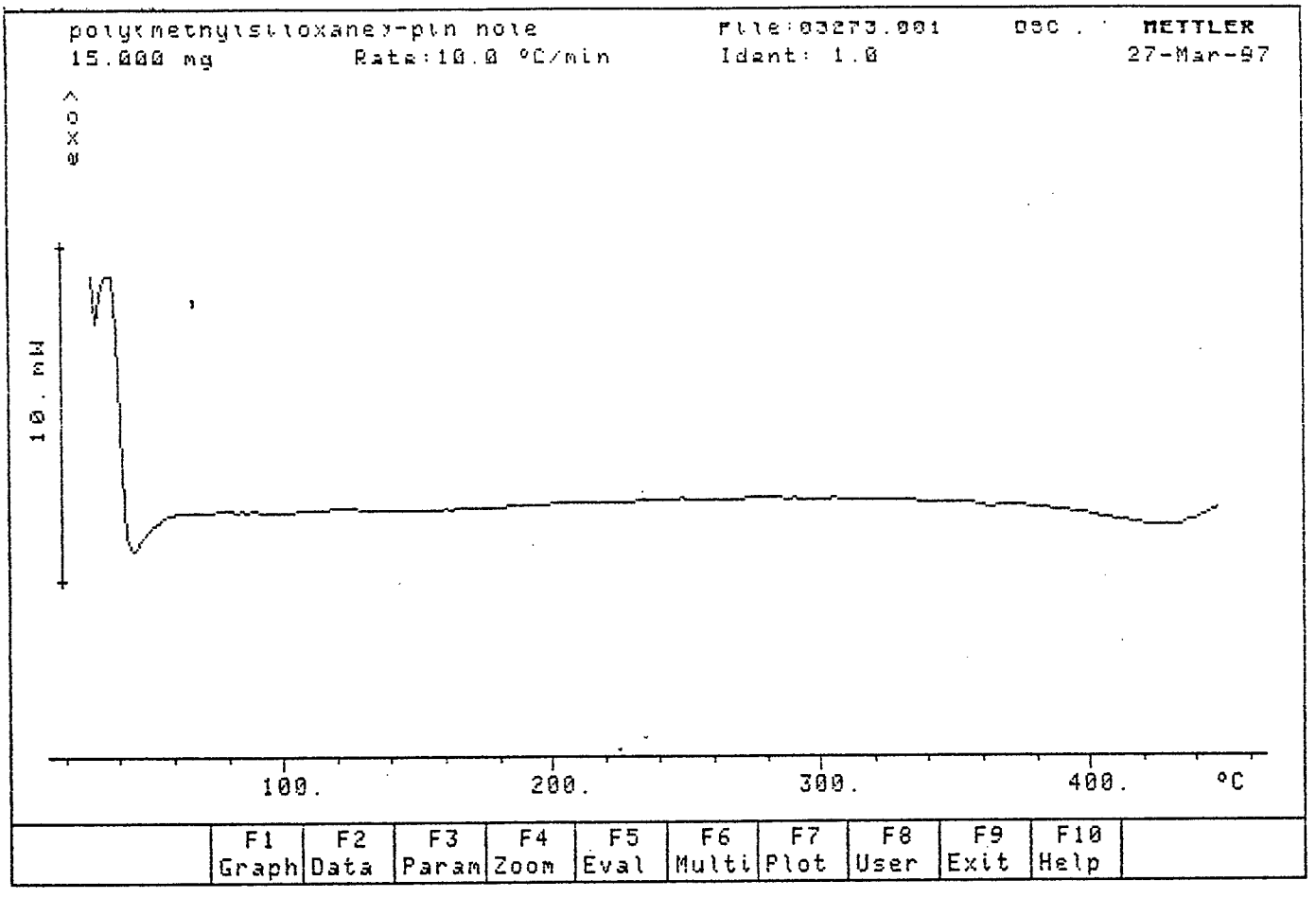
Propylene glycol

butyl ether



This document contains CONFIDENTIAL and PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

Poly(methylsiloxane)

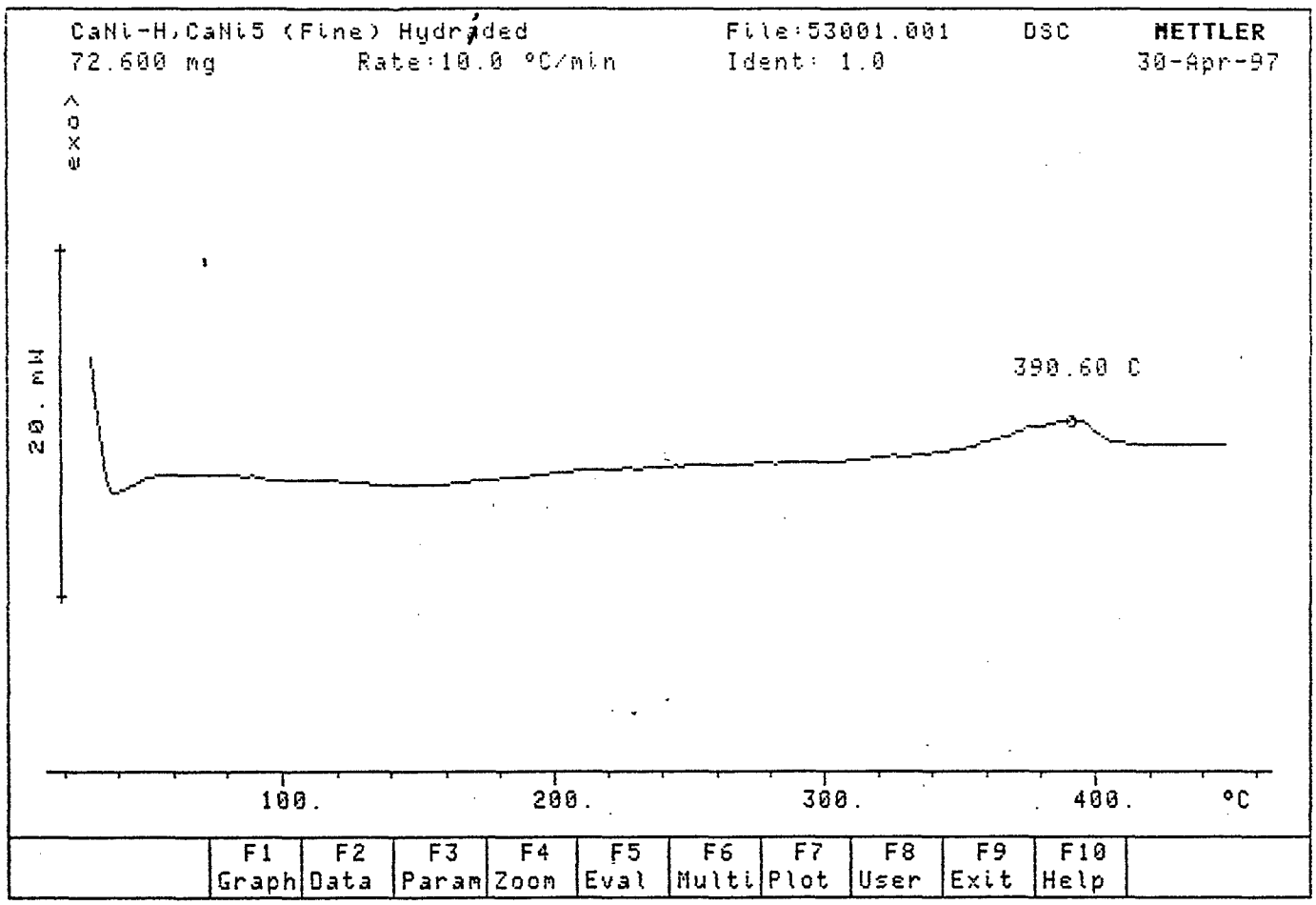


This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

CaNi-H (fine)

CaNi5 hydride

sent to Army ICD

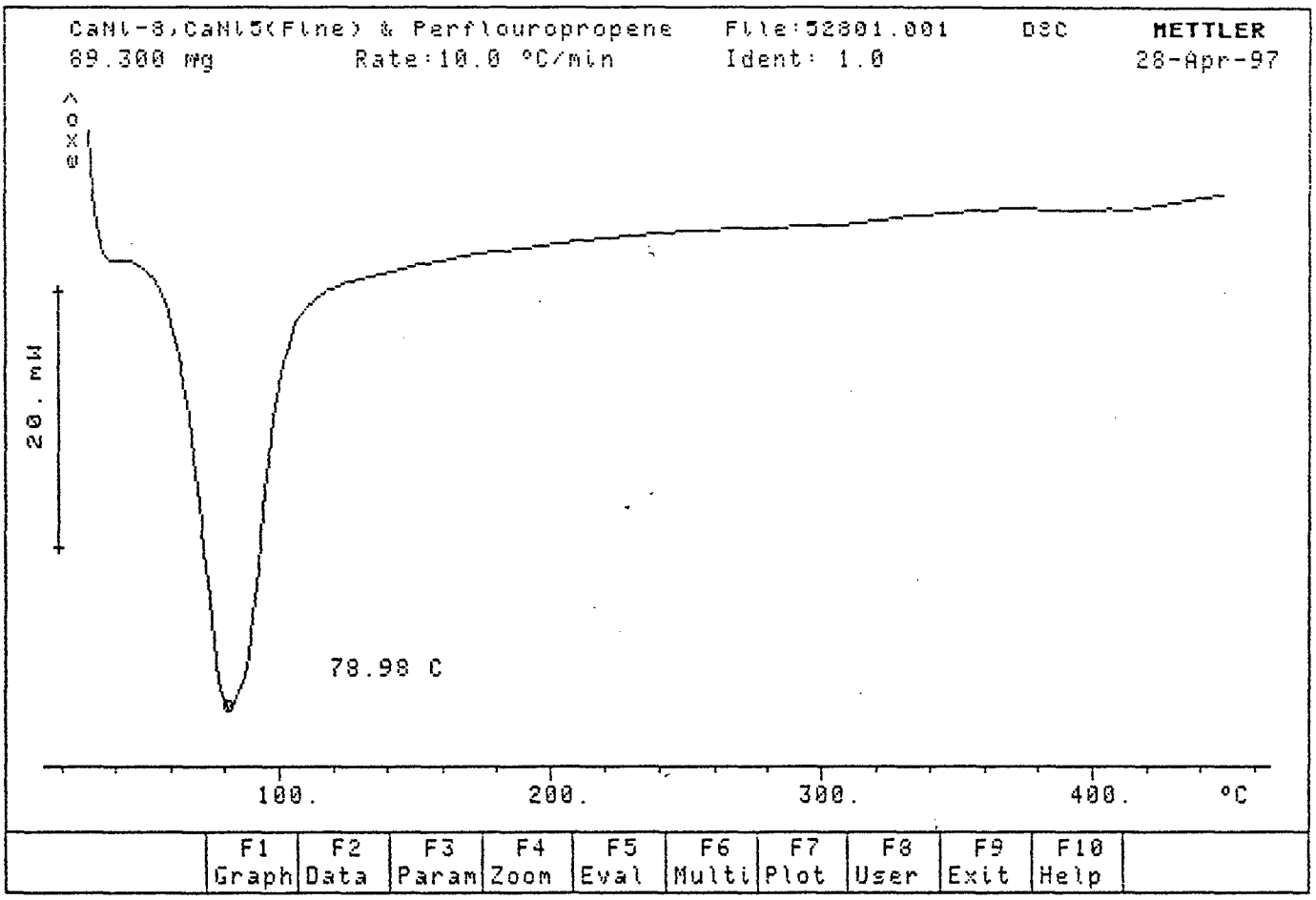


This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

CaNi-8 (fine)

CaNi5&PFP

sent to Army ICD

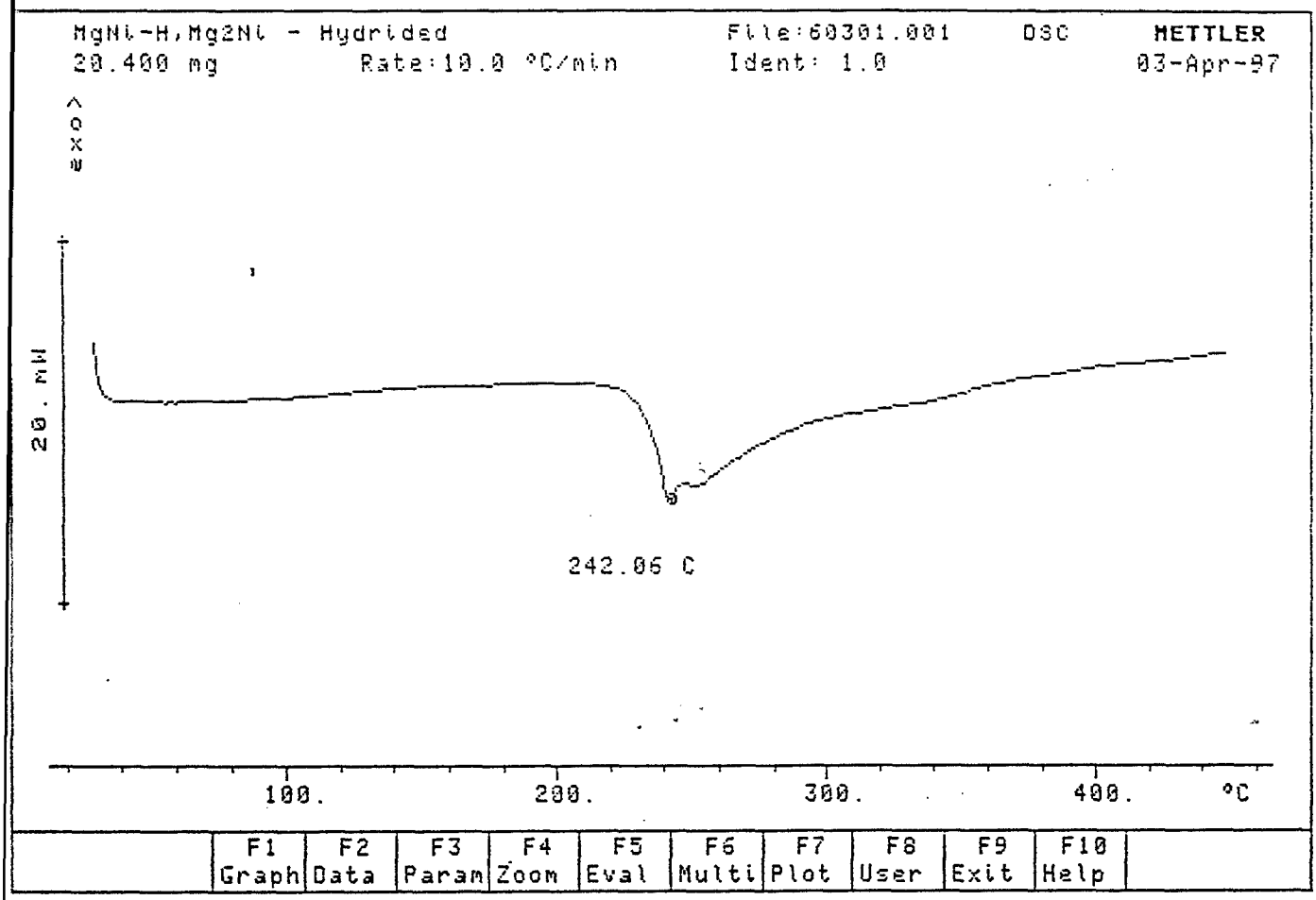


This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

MgNi-H (fine)

Mg2Ni hydride

sent to Army ICD

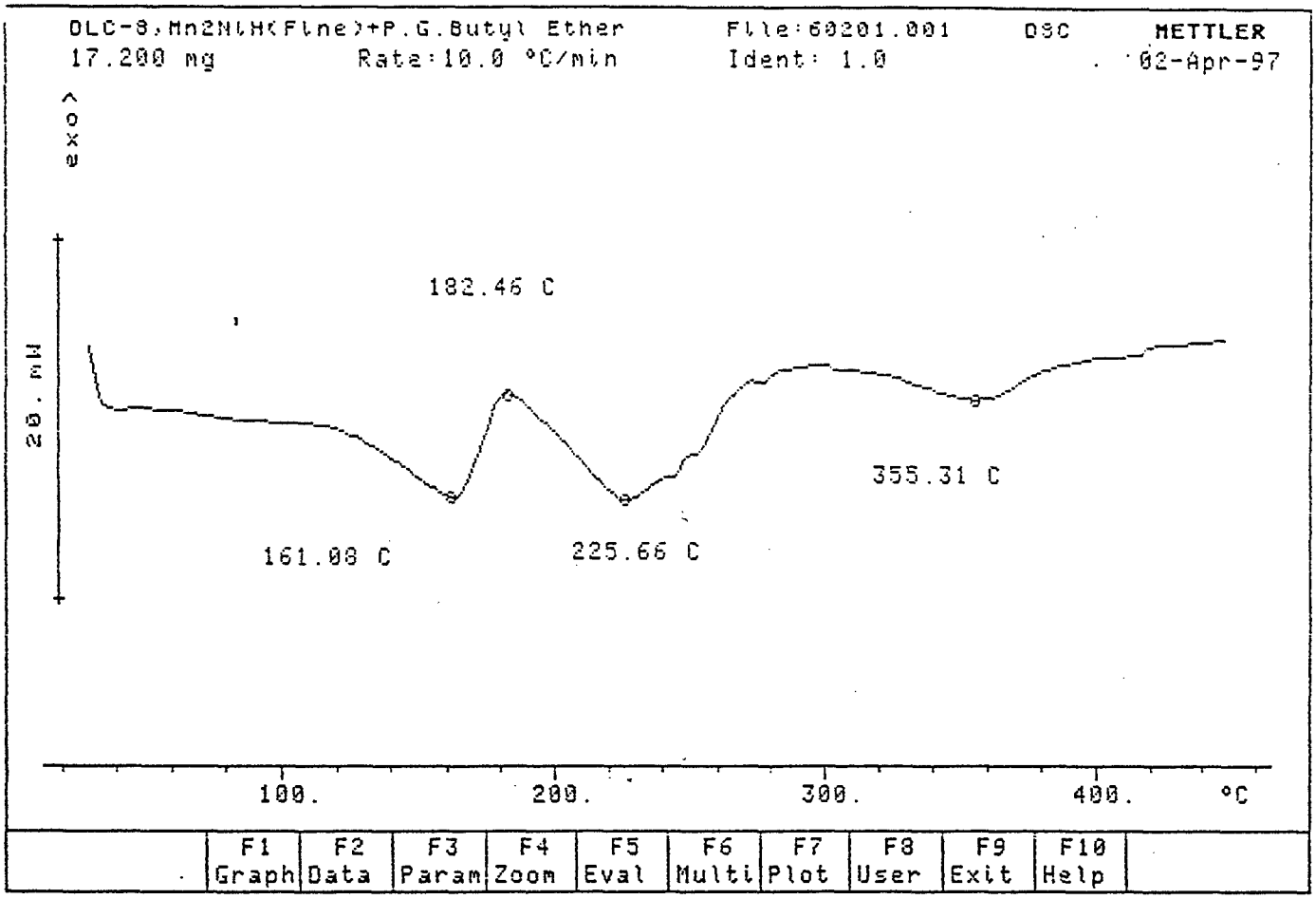


This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

DLC-8 (fine)

Mg2Ni&PGBE

sent to Army ICD

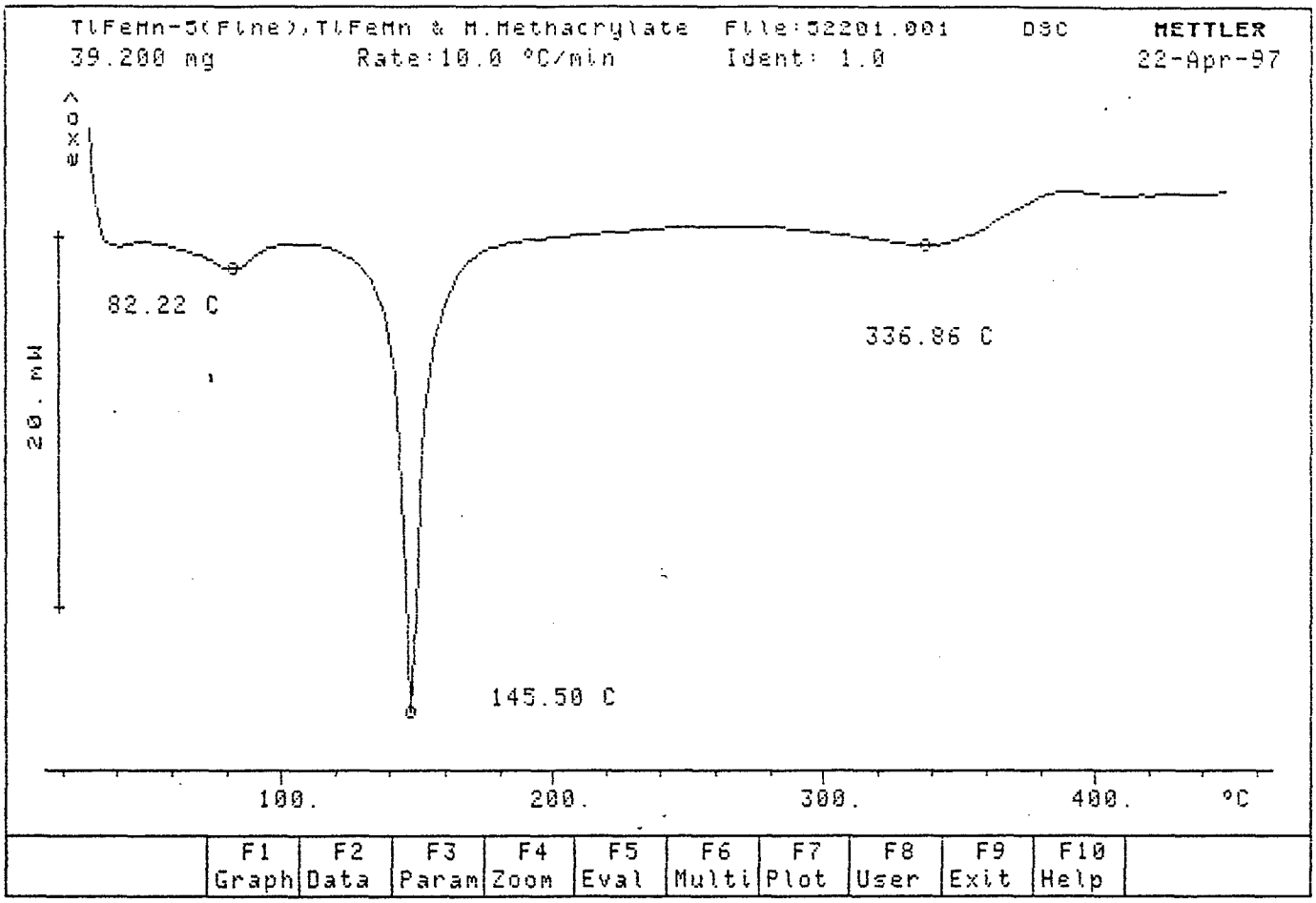


This document contains [redacted] and PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

TiFeMn-5 (fine)

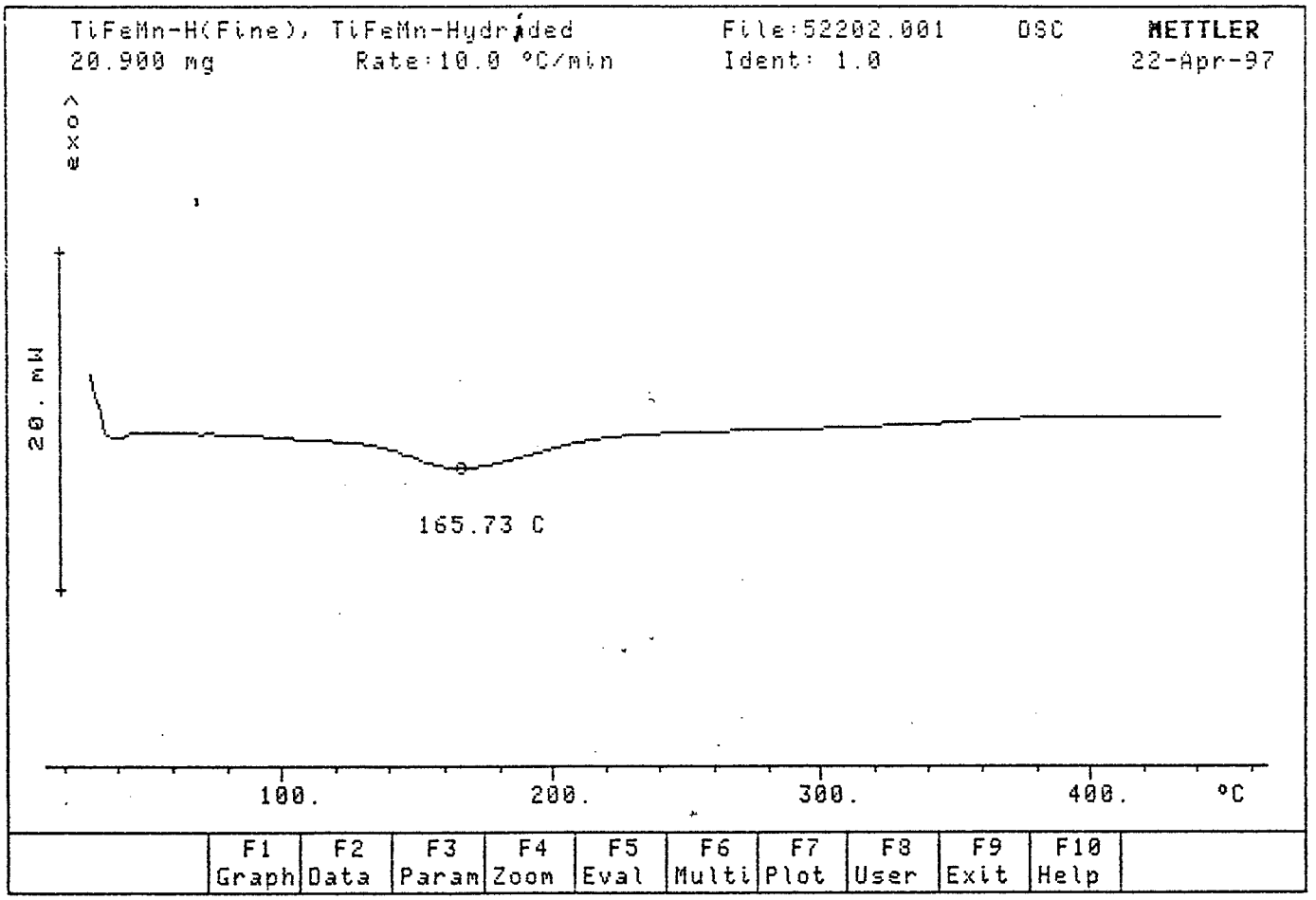
TiFeMn & MM

sent to Army ICD



This document contains [redacted] and PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

TiFeMn-H (fine)
TiFeMn hydride
sent to Army ICD



This document contains [redacted] and PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

This document contains [redacted] PROPRIETARY information of Mainstream Engineering Corporation and cannot be used, duplicated or disclosed, in whole or in part, except with the express written permission of Mainstream.

APPENDIX D - LC RAW DATA AND STATISTICS

TDE HPLC:

- CaNi-8
- MgNi-5
- MgNi-8
- MgNi-4
- MgNi-3
- TiFeMn-5

DMMP HPLC:

- CaNi-8
- DLC-8
- MgNi-8
- MgNi-3
- TiFeMn-5
- TiFeMn-5

OTHER HPLC:

- molecular sieve baseline
- molecular sieve with MM
- molecular sieve with PGBE

ASKIN RESULTS

MAINSTREAM Engineering Corporation

DATE 5/7/97
ANALYST
SIGNATURE

CaNi5 - no treatment with acetonitrile extraction

Date Analyzed	Actual Percent thiodiethano	Determined Percent thiodiethano	Percent Recovered
3/25/97	10.00%	7.95%	79.51%
3/25/97	10.00%	7.66%	76.58%
3/25/97	10.00%	9.45%	94.48%
3/25/97	10.00%	10.18%	101.77%
3/25/97	10.00%	9.85%	98.52%
3/25/97	2.32%	2.03%	87.38%
3/25/97	2.32%	2.04%	87.83%
3/25/97	2.32%	2.06%	88.98%
3/27/97	1.40%	1.38%	98.49%
3/31/97	2.02%	1.80%	89.31%
3/31/97	2.02%	1.93%	95.66%
3/31/97	2.02%	1.81%	89.39%
3/31/97	2.02%	2.00%	98.78%
3/31/97	2.02%	1.75%	86.65%
4/1/97	1.60%	1.39%	86.92%
4/1/97	1.60%	1.36%	84.74%
4/1/97	1.60%	1.40%	87.56%
4/1/97	1.60%	1.37%	85.87%
4/1/97	1.60%	1.35%	84.68%
4/1/97	1.60%	1.38%	86.34%

ASKIN RESULTS

MAINSTREAM

DATE 5/7/97

ANALYST CAN

SIGNATURE

CaNi5 -Hydrogenated, experiment #8

Date Analyzed	Actual Percent Thiodiethanol	Determined Percent Thiodiethanol	Percent Recovered
3/31/97	2.41%	2.26%	93.63%
3/31/97	2.41%	2.05%	84.89%
3/31/97	2.41%	2.08%	86.22%
3/31/97	2.41%	2.06%	85.40%
3/31/97	2.41%	2.08%	86.42%
3/31/97	2.41%	2.08%	86.18%
3/31/97	2.41%	2.12%	88.16%
3/31/97	2.41%	2.18%	90.55%
3/31/97	1.42%	1.22%	85.57%
3/31/97	1.42%	1.24%	87.52%
3/31/97	1.42%	1.22%	85.81%
4/1/97	1.42%	1.35%	95.16%
4/1/97	1.42%	1.39%	97.92%
4/1/97	1.42%	1.43%	100.68%
4/1/97	1.42%	1.35%	95.31%
4/1/97	1.42%	1.33%	93.53%
4/1/97	2.05%	2.02%	98.70%
4/1/97	2.05%	2.03%	98.94%
4/1/97	2.05%	1.91%	92.98%
4/1/97	2.05%	1.87%	91.33%

ASKIN RESULTS - Statistical Summary

DATE 5/7/97

ANALYST CAN

SIGNATURE

MAINSTREAM Engineering Corporation

CaNi5 -Hydrogenated, experiment #8

Anova: Single Factor

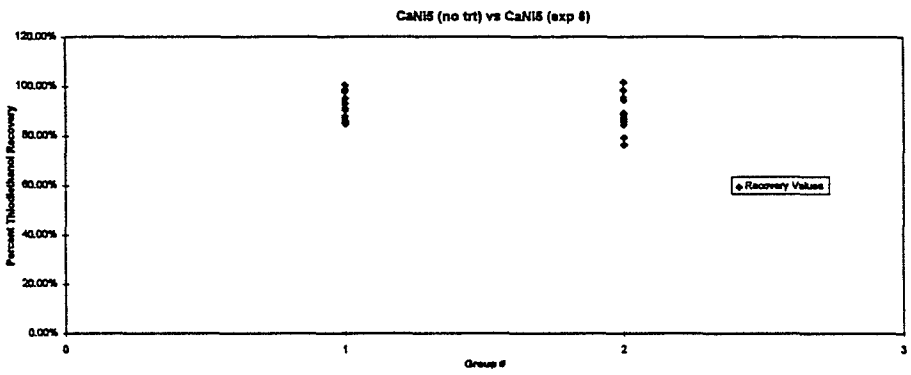
SUMMARY

Groups	Count	Sum	Average	Variance
1: CaNi5 acet extr	20	18.24887436	0.912443718	0.002781894
2: CaNi5 exp 8	20	17.89444806	0.894722403	0.004336173

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.00314045	1	0.00314045	0.882388354	0.353481311	4.098168915
Within Groups	0.135243286	38	0.003559034			
Total	0.138383736	39				

Conclusion: There is no significant difference (95% probability) between groups



ASKIN RESULTS

MAINSTREAM

DATE 5/9/97
ANALYST CAN
SIGNATURE

Mg2Ni -No treatment, extracted with water instead of acetonitrile

Date Analyzed	Actual Percent Thiodiethanol	Determined Percent Thiodiethanol	Percent Recovered
04/04/97	1.48%	2.13%	144.03%
04/04/97	1.48%	2.17%	146.50%
04/04/97	1.48%	2.20%	148.52%
04/04/97	1.48%	2.13%	143.96%
04/04/97	1.48%	2.11%	142.85%
04/04/97	1.48%	2.15%	145.73%
04/04/97	1.48%	2.10%	142.09%
04/04/97	1.48%	2.20%	148.58%
04/04/97	1.48%	2.21%	149.76%
04/04/97	1.68%	2.34%	139.11%
04/04/97	1.68%	2.32%	138.10%
04/04/97	1.68%	2.37%	141.46%
04/04/97	1.68%	2.39%	142.55%
04/04/97	1.68%	2.33%	139.07%
04/04/97	1.68%	2.39%	142.65%

ASKIN RESULTS

MAINSTREAM

DATE 5/9/97

ANALYST CAR

SIGNATURE

Mg2Ni -Experiment #5, extracted with water instead of acetonitrile

Date Analyzed	Actual Percent Thiodiethanol	Determined Percent Thiodiethanol	Percent Recovered
04/07/97	1.10%	1.45%	132.42%
04/07/97	1.10%	1.85%	168.95%
04/07/97	1.10%	1.43%	130.95%
04/07/97	1.10%	1.85%	169.16%
04/07/97	1.10%	1.45%	132.08%
04/07/97	1.10%	1.78%	162.49%
04/07/97	1.10%	1.43%	130.20%
04/07/97	1.10%	1.43%	130.74%
04/07/97	1.14%	1.65%	144.52%
04/07/97	1.14%	1.72%	150.19%
04/07/97	1.14%	1.73%	151.03%
04/07/97	1.14%	1.65%	144.43%
04/07/97	1.14%	1.70%	148.43%
04/07/97	1.14%	1.84%	160.49%
04/07/97	1.14%	1.85%	161.47%

ASKIN RESULTS - Statistical Summary

DATE 5/9/97

ANALYST TAN

SIGNATURE John Mayo

MAINSTREAM Engineering Corporation

Mg2Ni -Experiment #5, extracted with water instead of acetonitrile

Anova: Single Factor

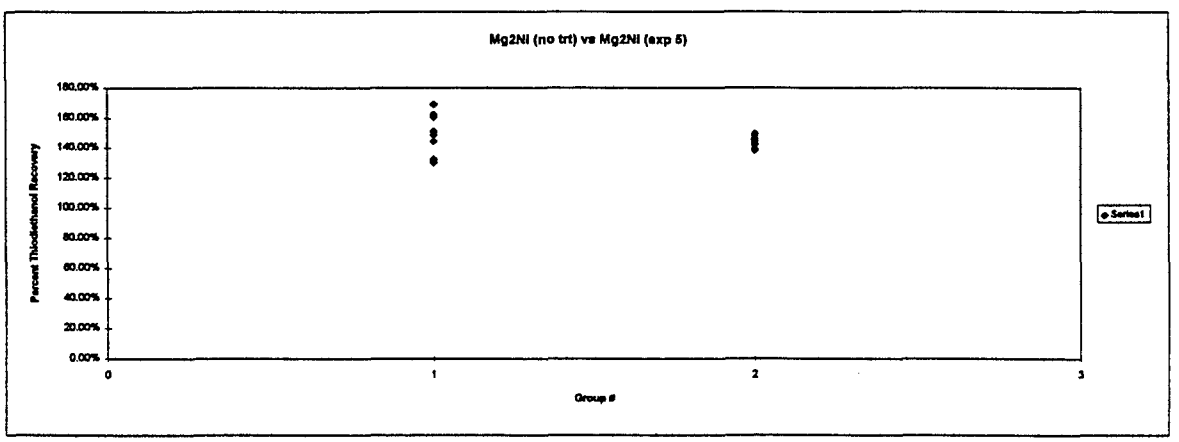
SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Column 1	15	22.17547921	1.47836528	0.020533008
Column 2	15	21.54972278	1.436648186	0.001289452

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.01305237	1	0.01305237	1.196232724	0.283396347	4.195982228
Within Groups	0.30551443	28	0.01091123			
Total	0.3185668	29				

Conclusion: There is no significant difference (95% probability) between groups



ASKIN RESULTS

MAINSTREAM

DATE 5/9/97

ANALYST TAM

SIGNATURE John Meyer

Mg2Ni -Hydrogenated, experiment #8

Date Analyzed	Actual Percent Thiodiethanol	Determined Percent Thiodiethanol	Percent Recovered
04/01/97	3.62%	4.30%	118.72%
04/02/97	3.62%	4.57%	126.13%
04/02/97	3.62%	4.78%	132.10%
04/02/97	3.62%	4.82%	133.15%
04/02/97	3.62%	4.65%	128.47%
04/02/97	3.62%	4.53%	125.09%
04/02/97	1.99%	2.57%	128.94%
04/02/97	1.99%	2.77%	138.86%
04/02/97	1.99%	2.56%	128.28%
04/02/97	1.99%	2.56%	128.35%
04/02/97	1.99%	2.61%	130.77%
04/02/97	1.99%	2.70%	135.73%
04/02/97	1.59%	2.06%	129.55%
04/02/97	1.59%	2.14%	134.66%
04/02/97	1.59%	2.12%	133.36%

ASKIN RESULTS

MAINSTREAM

DATE 5/9/97
ANALYST
SIGNATURE

Mg2Ni - no treatment with acetonitrile extraction

Date Analyzed	Actual Percent thiodiethanol	Determined Percent thiodiethanol	Percent Recovered
4/1/97	1.94%	2.46%	127.06%
4/1/97	1.94%	2.49%	128.43%
4/1/97	1.94%	2.42%	124.73%
4/1/97	1.94%	2.54%	130.94%
4/1/97	1.94%	2.60%	133.85%
4/1/97	1.94%	2.60%	133.77%
4/1/97	1.94%	2.50%	128.75%
4/1/97	2.18%	2.84%	130.31%
4/1/97	2.18%	2.98%	136.48%
4/1/97	2.18%	2.80%	128.51%
4/1/97	2.18%	2.82%	129.44%
4/1/97	2.18%	2.81%	128.77%
4/1/97	2.18%	2.78%	127.30%
4/1/97	2.18%	2.80%	128.44%
4/1/97	2.18%	2.77%	127.26%

ASKIN RESULTS - Statistical Summary

DATE 5/9/97

ANALYST JCN

SIGNATURE

MAINSTREAM Engineering Corporation

Mg2Ni -Hydrogenated, experiment #8

Anova: Single Factor

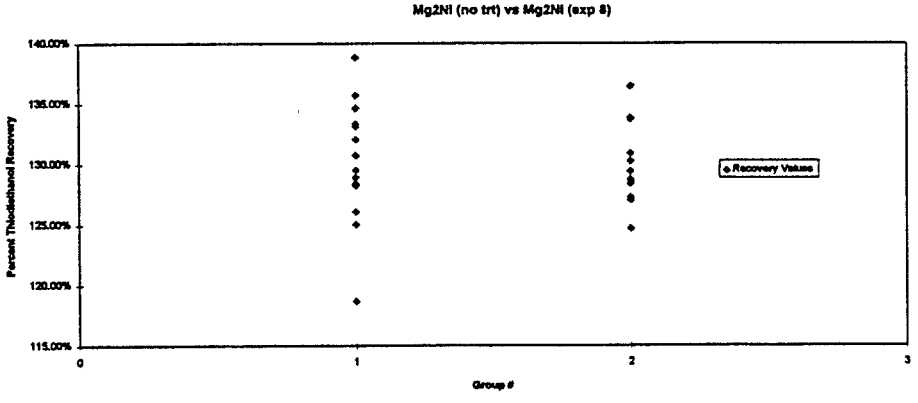
SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
1: Mg2Ni exp 8 acet ex	15	19.52165127	1.301443418	0.002390866
2: Mg2Ni no trt acet ex	15	19.44042844	1.296028563	0.000938323

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.000219905	1	0.000219905	0.132107182	0.718987075	4.195982228
Within Groups	0.046608649	28	0.001664595			
Total	0.046828554	29				

Conclusion: There is no significant difference (95% probability) between groups



ASKIN RESULTS - Statistical Summary

MAINSTREAM Engineering Corporation

DATE 5/9/97

ANALYST DAM

SIGNATURE John Mayer

Mg2Ni -Hydrogenated, experiment #4

Anova: Single Factor

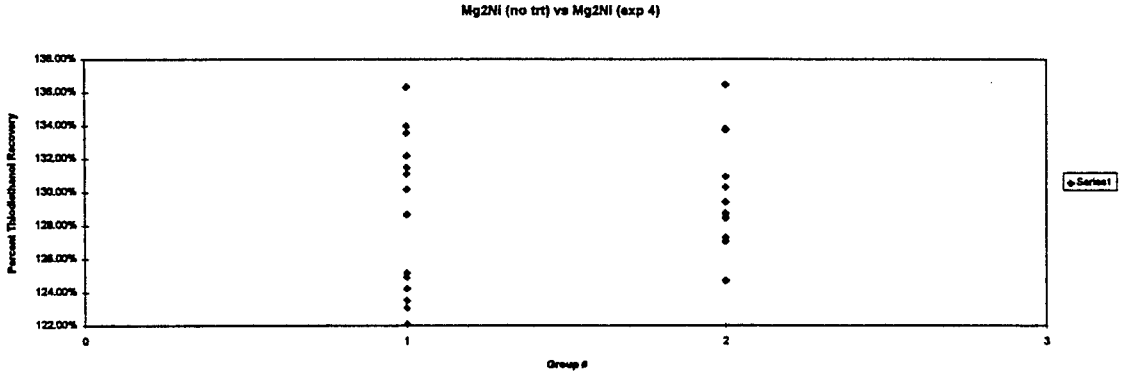
SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
1: Mg2Ni exp 3 acet ex	15	19.3461894	1.28974596	0.002234193
2: Mg2Ni no trt acet ex	15	19.44042844	1.296028563	0.000938323

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.000296033	1	0.000296033	0.186623624	0.669050371	4.195982228
Within Groups	0.04441523	28	0.001586258			
Total	0.044711263	29				

Conclusion: There is no significant difference (95% probability) between groups



ASKIN RESULTS

MAINSTREAM Engineering Corporation

DATE 5/9/97

ANALYST JAM

SIGNATURE John M Meyer

Mg2Ni -Hydrogenated, experiment #4

Date Analyzed	Actual Percent Thiodiethanol	Determined Percent Thiodiethanol	Percent Recovered
04/03/97	1.46%	1.82%	124.93%
04/03/97	1.46%	1.81%	124.24%
04/03/97	1.46%	1.78%	122.12%
04/03/97	1.46%	1.80%	123.54%
04/03/97	1.46%	1.91%	131.10%
04/03/97	1.46%	1.92%	131.49%
04/03/97	1.46%	1.83%	125.19%
04/03/97	1.46%	1.90%	130.17%
04/03/97	1.46%	1.80%	123.08%
04/03/97	1.52%	1.95%	128.69%
04/03/97	1.52%	2.03%	133.97%
04/03/97	1.52%	2.07%	136.34%
04/03/97	1.52%	2.03%	133.57%
04/03/97	1.52%	2.03%	134.00%
04/03/97	1.52%	2.01%	132.20%

ASKIN RESULTS

MAINSTREAM

DATE 5/9/97

ANALYST DAN

SIGNATURE

Mg2Ni -Hydrogenated, experiment #3

Date Analyzed	Actual Percent Thiodiethanol	Determined Percent Thiodiethanol	Percent Recovered
04/03/97	2.67%	3.42%	127.88%
04/03/97	2.67%	3.49%	130.78%
04/03/97	2.67%	3.89%	145.56%
04/03/97	2.67%	3.67%	137.40%
04/03/97	2.67%	3.90%	146.00%
04/03/97	2.67%	3.82%	142.83%
04/03/97	2.67%	3.60%	134.85%
04/03/97	2.67%	3.73%	139.74%
04/03/97	1.48%	2.00%	134.77%
04/03/97	1.48%	1.94%	131.22%
04/03/97	1.48%	2.00%	134.90%
04/03/97	1.48%	2.00%	134.89%
04/03/97	1.48%	1.91%	129.06%
04/03/97	1.48%	2.00%	135.25%
04/03/97	1.48%	1.90%	128.47%

ASKIN RESULTS - Statistical Summary

MAINSTREAM Engineering Corporation

DATE 5/9/97

ANALYST TAN

SIGNATURE

Mg2Ni -Hydrogenated, experiment #3

Anova: Single Factor

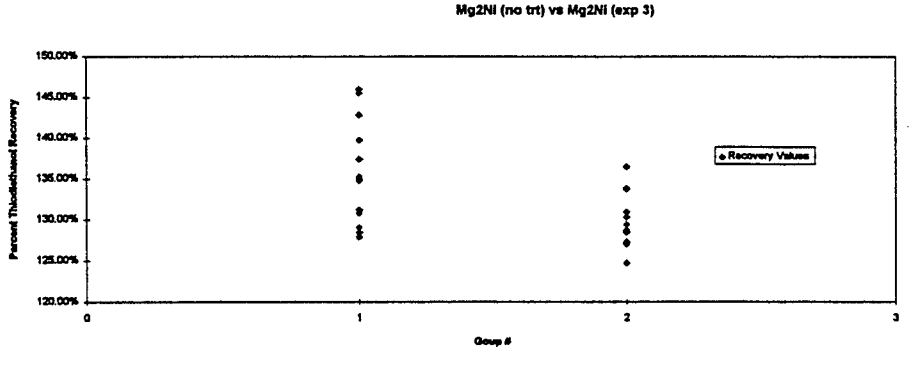
SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
1: Mg2Ni exp 8 acet ex	15	20.33602104	1.355734736	0.003413639
2: Mg2Ni exp 3	15	19.44042844	1.296028563	0.000938323

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.026736203	1	0.026736203	12.2869642	0.001554983	4.195982228
Within Groups	0.060927474	28	0.002175981			
Total	0.087663678	29				

Conclusion: There is a significant difference (95% probability) between groups



ASKIN RESULTS

MAINSTREAM Engineering Corporation

DATE 5/15/97
ANALYST
SIGNATURE

TiFeMn (no trt) water extraction

Date Analyzed	Actual Percent thiodiethano	Determined Percent thiodiethano	Percent Recovered
5/14/97	2.33%	2.95%	126.88%
5/14/97	2.33%	2.91%	125.20%
5/14/97	2.33%	3.04%	130.50%
5/14/97	2.33%	2.90%	124.53%
5/14/97	2.33%	2.96%	127.05%
5/14/97	2.33%	2.95%	126.66%
5/14/97	2.33%	2.88%	123.83%
5/14/97	2.33%	2.87%	123.46%
5/14/97	2.33%	2.88%	123.86%
5/14/97	2.33%	2.91%	125.20%
5/15/97	2.85%	3.62%	127.30%
5/15/97	2.85%	3.61%	126.66%
5/15/97	2.85%	3.56%	125.21%
5/15/97	2.85%	3.60%	126.53%
5/15/97	2.85%	3.61%	126.92%

ASKIN RESULTS

MAINSTREAM

DATE 5/15/97

ANALYST TAM

SIGNATURE John Meyer

TiFeMn (exp #5) water extraction

Date Analyzed	Actual Percent Thiodiethanol	Determined Percent Thiodiethanol	Percent Recovered
5/14/97	2.54%	2.56%	100.84%
5/14/97	2.54%	2.53%	99.64%
5/14/97	2.54%	2.61%	102.82%
5/14/97	2.54%	2.54%	100.18%
5/14/97	2.54%	2.58%	101.45%
5/14/97	2.54%	2.61%	102.71%
5/14/97	2.54%	2.59%	101.89%
5/15/97	2.54%	2.56%	100.99%
5/15/97	2.54%	2.61%	102.88%
5/15/97	2.54%	2.65%	104.24%
5/15/97	2.37%	2.16%	91.13%
5/15/97	2.37%	2.16%	91.00%
5/15/97	2.37%	2.14%	90.30%
5/15/97	2.37%	2.11%	89.22%
5/15/97	2.37%	2.17%	91.75%

ASKIN RESULTS - Statistical Summary

DATE 5/15/77
ANALYST JAM
SIGNATURE John [illegible]

MAINSTREAM
Engineering Corporation

TiFeMn (exp #5) water extraction

Anova: Single Factor

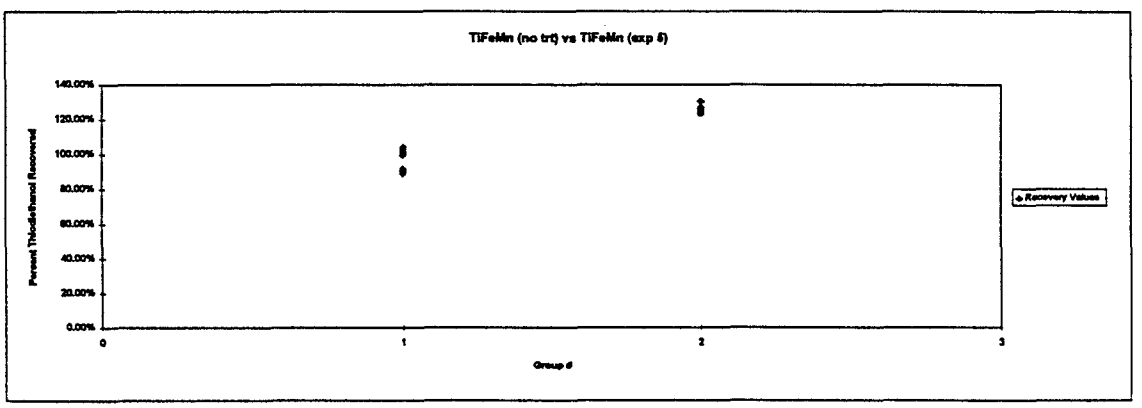
SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
1: TiFeMn exp 5	15	14.71048853	0.980699236	0.003080259
2: TiFeMn (no trt)	15	18.89782227	1.259854818	0.000325951

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.584458795	1	0.584458795	343.1725019	2.99567E-17	4.195982228
Within Groups	0.047686939	28	0.001703105			
Total	0.632145734	29				

Conclusion: There is a significant difference (95% probability) between groups



ASKIN RESULTS

MAINSTREAM Engineering Corporation

DATE 5/15/97
ANALYST TAN
SIGNATURE John A. Tegna

TiFeMn (no trt) water extraction

Date Analyzed	Actual Percent thiodiethano	Determined Percent thiodiethano	Percent Recovered
5/14/97	2.33%	2.95%	126.88%
5/14/97	2.33%	2.91%	125.20%
5/14/97	2.33%	3.04%	130.50%
5/14/97	2.33%	2.90%	124.53%
5/14/97	2.33%	2.96%	127.05%
5/14/97	2.33%	2.95%	126.66%
5/14/97	2.33%	2.88%	123.83%
5/14/97	2.33%	2.87%	123.46%
5/14/97	2.33%	2.88%	123.86%
5/14/97	2.33%	2.91%	125.20%

ASKIN RESULTS

MAINSTREAM

DATE 5/15/97

ANALYST TAN

SIGNATURE

TiFeMn (exp #5) water extraction

Date Analyzed	Actual Percent Thiodiethanol	Determined Percent Thiodiethanol	Percent Recovered
5/14/97	2.54%	2.56%	100.84%
5/14/97	2.54%	2.53%	99.64%
5/14/97	2.54%	2.61%	102.82%
5/14/97	2.54%	2.54%	100.18%
5/14/97	2.54%	2.58%	101.45%
5/14/97	2.54%	2.61%	102.71%
5/14/97	2.54%	2.59%	101.89%
5/14/97	2.54%	2.56%	100.99%
5/14/97	2.54%	2.61%	102.88%
5/14/97	2.54%	2.65%	104.24%

ASKIN RESULTS - Statistical Summary

DATE 5/15/97

ANALYST DAM

SIGNATURE

MAINSTREAM Engineering Corporation

TiFeMn (exp #5) water extraction

Anova: Single Factor [1]

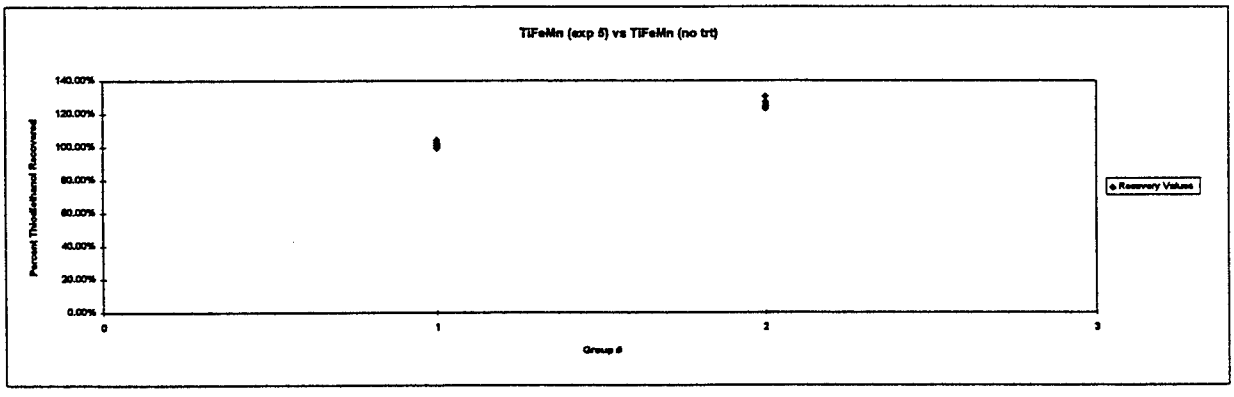
SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
1: TiFeMn (exp 5)	10	10.17647834	1.017647834	0.00019941
2: TiFeMn (no trt)	10	12.57173597	1.257173597	0.000455106

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.286862955	1	0.286862955	876.5647261	1.01202E-16	4.413863053
Within Groups	0.005890647	18	0.000327258			
Total	0.292753601	19				

Conclusion: There is a significant difference (95% probability) between groups



ASKIN RESULTS

MAINSTREAM Engineering Corporation

DATE 5/7/97

ANALYST TRN

SIGNATURE John Meyer

Calcium Nickel - Experiment #8

Date Analyzed	Actual Percent DMMP	Determined Percent DMMP	Percent Recovered
3/26/97	1.73%	0.33%	19.21%
3/26/97	1.73%	2.82%	162.78%
3/26/97	1.73%	0.27%	15.46%
3/27/97	3.11%	2.30%	73.87%
3/27/97	3.11%	3.21%	103.33%
3/27/97	3.11%	2.09%	67.27%
3/27/97	3.11%	2.10%	67.63%
3/27/97	3.11%	1.10%	35.26%
3/27/97	3.11%	1.55%	49.69%
3/27/97	3.11%	1.90%	61.19%
3/27/97	3.51%	-0.08%	-2.33%
3/27/97	3.51%	0.73%	20.67%
3/27/97	3.51%	-0.06%	-1.75%
3/27/97	3.51%	0.21%	6.03%
3/27/97	3.51%	0.55%	15.78%
3/27/97	3.51%	-0.19%	-5.35%
3/27/97	3.51%	-0.22%	-6.36%
3/27/97	3.51%	-0.32%	-9.11%
3/27/97	3.51%	1.51%	43.01%
3/27/97	3.51%	-0.04%	-1.05%

ASKIN RESULTS

MAINSTREAM Engineering Corporation

DATE 5/7/97
ANALYST DAN
SIGNATURE John A Payne

Calcium Nickel - No Treatment

Date Analyzed	Actual Percent DMMP	Determined Percent DMMP	Percent Recovered
3/26/97	16.20%	17.29%	106.74%
3/26/97	16.20%	17.80%	109.89%
3/26/97	16.20%	16.39%	101.18%
3/26/97	1.44%	2.09%	145.42%
3/26/97	1.44%	1.77%	122.77%
3/27/97	0.84%	1.38%	165.58%
3/27/97	0.84%	0.84%	101.05%
3/27/97	0.84%	0.95%	113.36%
3/27/97	0.84%	0.51%	61.08%
3/27/97	0.84%	0.67%	80.38%
3/27/97	1.75%	2.08%	118.81%
3/27/97	1.75%	1.75%	100.08%
3/27/97	1.75%	1.28%	73.10%
3/27/97	1.75%	1.61%	92.05%
3/27/97	1.75%	0.95%	54.43%
3/27/97	1.75%	1.17%	66.86%
3/27/97	1.75%	1.37%	78.40%
3/27/97	2.05%	3.43%	167.24%
3/27/97	2.05%	2.95%	144.00%
3/27/97	2.05%	2.65%	129.32%

ASKIN RESULTS - Statistical Summary

DATE 5/7/97

ANALYST DAM

SIGNATURE

MAINSTREAM Engineering Corporation

Calcium Nickel - Experiment #8

Anova: Single Factor

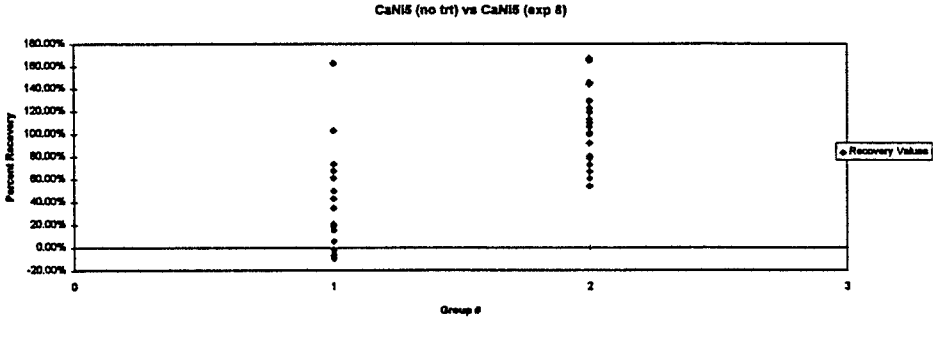
SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
1: CaNi Exp #8	20	7.152280708	0.357614035	0.194423586
2: CaNi No trt acet extr	20	21.31743452	1.065871726	0.107040358

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	5.016289565	1	5.016289565	33.27953256	1.18165E-06	4.098168915
Within Groups	5.72781493	38	0.150731972			
Total	10.74410449	39				

Conclusion: There is a significant difference (95% probability) between groups



ASKIN RESULTS

MAINSTREAM Engineering Corporation

DATE 5/7/97
ANALYST GAN
SIGNATURE

Mg2Ni - no treatment with water extraction

Date Analyzed	Actual Percent DMMP	Determined Percent DMMP	Percent Recovered
4/30/97	1.61%	2.61%	162.63%
4/30/97	1.61%	2.81%	175.00%
4/30/97	1.61%	4.89%	304.48%
4/30/97	1.61%	3.75%	233.45%
4/30/97	1.61%	4.03%	250.64%
4/30/97	1.61%	5.01%	311.60%
4/30/97	1.61%	3.33%	207.61%
4/30/97	1.61%	4.51%	280.49%
4/30/97	1.61%	4.52%	281.22%
4/30/97	1.61%	4.91%	305.71%
4/30/97	1.61%	4.78%	297.57%
4/30/97	1.61%	7.20%	448.00%
4/30/97	1.61%	5.21%	324.16%
4/30/97	1.61%	5.16%	321.39%
4/30/97	1.61%	5.68%	353.31%
4/30/97	1.61%	4.26%	265.08%
4/30/97	1.61%	5.02%	312.75%
4/30/97	1.61%	4.35%	270.51%
4/30/97	1.61%	4.88%	303.74%
4/30/97	1.61%	5.07%	315.44%

ASKIN RESULTS

MAINSTREAM Engineering Corporation

DATE 5/7/97

ANALYST CAN

SIGNATURE John M. Cuya

Mg2Ni - DLC-8 water extraction

Date Analyzed	Actual Percent DMMP	Determined Percent DMMP	Percent Recovered
5/1/97	3.22%	3.72%	115.46%
5/1/97	3.22%	5.67%	175.82%
5/1/97	3.22%	7.64%	236.96%
5/1/97	3.22%	5.32%	165.20%
5/1/97	3.22%	6.30%	195.34%
5/1/97	3.22%	6.01%	186.36%
5/1/97	3.22%	7.58%	235.24%
5/1/97	3.22%	7.76%	240.64%
5/1/97	3.22%	8.10%	251.19%
5/1/97	3.22%	11.66%	361.75%
5/1/97	3.22%	9.02%	279.83%
5/1/97	3.22%	9.54%	295.92%
5/1/97	3.22%	4.19%	130.05%
5/1/97	3.22%	9.29%	288.23%
5/5/97	1.85%	0.00%	0.00%
5/5/97	1.85%	0.00%	0.00%
5/5/97	1.85%	0.00%	0.00%
5/5/97	1.85%	0.00%	0.00%
5/5/97	1.85%	0.00%	0.00%
5/5/97	1.85%	0.00%	0.00%

ASKIN RESULTS - Statistical Summary

DATE 5/7/97

ANALYST AM

SIGNATURE

MAINSTREAM Engineering Corporation

Mg2Ni - DLC-8 water extraction

Anova: Single Factor

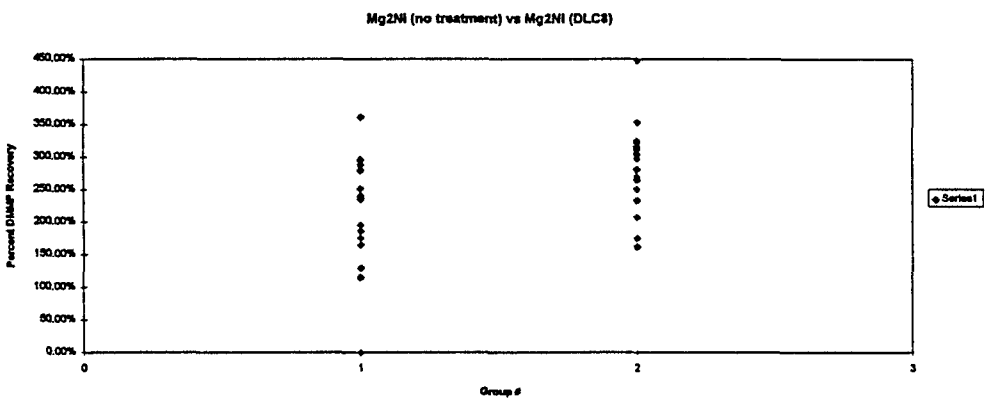
SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
1. Mg2Ni DLC 8	20	31.57990039	1.57899502	1.447359357
2. Mg2Ni no trt water e	20	57.24787258	2.862393629	0.396458393

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	16.4711199	1	16.4711199	17.86632101	0.000143241	4.098168915
Within Groups	35.03253726	38	0.921908875			
Total	51.50365717	39				

Conclusion: There is a significant difference (95% probability) between groups



ASKIN RESULTS

MAINSTREAM Engineering Corporation

DATE 5/7/97
ANALYST [illegible]
SIGNATURE [illegible]

Mg2Ni - no treatment with acetonitrile extraction

Date Analyzed	Actual Percent DMMP	Determined Percent DMMP	Percent Recovered
4/15/97	1.11%	0.77%	69.76%
4/15/97	1.11%	0.19%	16.91%
4/15/97	2.73%	4.31%	157.94%
4/15/97	2.73%	2.50%	91.36%
4/15/97	2.73%	3.99%	145.96%
4/15/97	2.73%	2.17%	79.56%
4/15/97	2.73%	3.19%	116.76%
4/15/97	2.73%	2.31%	84.59%
4/15/97	2.73%	2.31%	84.52%
4/15/97	2.73%	2.31%	84.39%
4/15/97	2.73%	1.93%	70.76%
4/15/97	2.73%	2.01%	73.50%
4/15/97	2.73%	3.26%	119.18%
4/15/97	2.73%	2.19%	80.13%
4/15/97	2.16%	4.33%	200.34%
4/15/97	2.16%	4.09%	189.22%
4/15/97	3.27%	3.91%	119.61%
4/15/97	3.27%	3.56%	108.84%
4/15/97	3.27%	3.03%	92.66%
4/15/97	3.27%	3.88%	118.64%

ASKIN RESULTS

MAINSTREAM Engineering Corporation

DATE 5/7/97

ANALYST GSM

SIGNATURE

Mg2Ni -Hydrogenated, experiment #8

Date Analyzed	Actual Percent DMMP	Determined Percent DMMP	Percent Recovered
4/15/97	2.78%	5.74%	206.65%
4/15/97	2.78%	5.02%	180.91%
4/15/97	2.78%	5.79%	208.43%
4/15/97	2.78%	5.65%	203.51%
4/15/97	2.78%	5.76%	207.32%
4/16/97	2.83%	2.57%	90.74%
4/16/97	2.83%	2.64%	93.10%
4/16/97	2.83%	2.64%	93.10%
4/16/97	2.83%	2.36%	83.31%
4/16/97	2.83%	2.35%	83.06%
4/16/97	2.83%	3.13%	110.47%
4/16/97	2.83%	2.37%	83.51%
4/16/97	2.83%	2.57%	90.55%
4/16/97	2.83%	2.23%	78.62%
4/16/97	2.83%	2.22%	78.53%
4/16/97	2.83%	3.24%	114.49%
4/16/97	2.83%	2.48%	87.38%
4/16/97	2.83%	2.49%	87.88%
4/16/97	2.83%	4.25%	150.13%
4/16/97	2.83%	2.62%	92.32%

ASKIN RESULTS - Statistical Summary

MAINSTREAM Engineering Corporation

DATE 5/7/97

ANALYST TOM

SIGNATURE

Mg2Ni -Hydrogenated, experiment #8

Anova: Single Factor

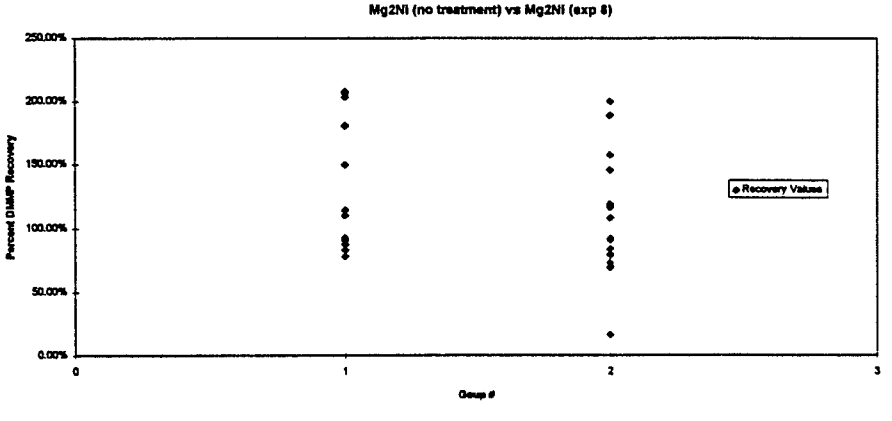
SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
1: Ng2Ni exp #8	20	24.24026663	1.212013331	0.253378667
2: Mg2Ni - No trt acet	20	21.04625253	1.052312627	0.186569912

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.255043151	1	0.255043151	1.159422546	0.288374023	4.098168915
Within Groups	8.359023009	38	0.21997429			
Total	8.61406616	39				

Conclusion: There is no significant difference (95% probability) between groups



ASKIN RESULTS

MAINSTREAM Engineering Corporation

DATE 5/7/97

ANALYST CAR

SIGNATURE

Mg2Ni -Hydrogenated, experiment #3

Date Analyzed	Actual Percent DMMP	Determined Percent DMMP	Percent Recovered
4/16/97	1.85%	4.28%	232.03%
4/16/97	1.85%	4.54%	246.03%
4/16/97	1.85%	2.87%	155.28%
4/16/97	1.85%	2.59%	140.57%
4/16/97	1.85%	2.79%	151.09%
4/16/97	1.85%	2.63%	142.25%
4/16/97	1.85%	2.44%	132.45%
4/16/97	1.85%	2.47%	133.60%
4/16/97	1.85%	3.11%	168.42%
4/16/97	1.85%	2.51%	136.14%
4/24/97	2.54%	6.26%	246.41%
4/24/97	2.54%	9.50%	374.01%
4/24/97	2.54%	5.82%	228.93%
4/24/97	2.54%	8.14%	320.28%
4/24/97	2.54%	7.80%	307.19%
4/24/97	2.54%	8.07%	317.73%
4/24/97	2.54%	8.78%	345.61%
4/24/97	2.54%	9.03%	355.38%
4/24/97	2.54%	9.46%	372.43%
4/24/97	2.54%	6.84%	269.12%

ASKIN RESULTS - Statistical Summary

DATE 5/7/97

ANALYST DAM

SIGNATURE

MAINSTREAM Engineering Corporation

Mg2Ni -Hydrogenated, experiment #3

Anova: Single Factor

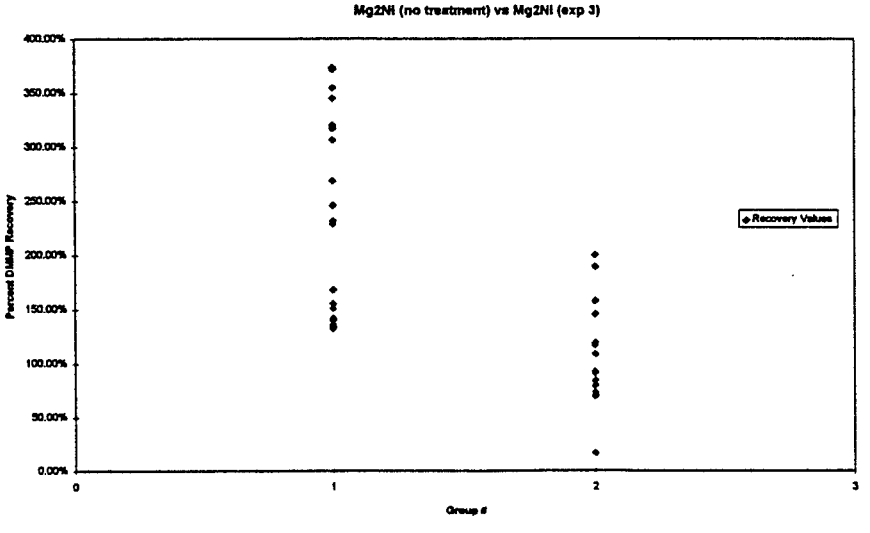
SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
1: Mg2Ni exp 3	20	47.74938149	2.387469075	0.79666308
2: Mg2Ni - No trt acet	20	21.04625253	1.052312627	0.186569912

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	17.82642741	1	17.82642741	36.26084061	5.31566E-07	4.098168915
Within Groups	18.68142686	38	0.491616496			
Total	36.50785427	39				

Conclusion: There is a significant difference (95% probability) between groups



ASKIN RESULTS

MAINSTREAM Engineering Corporation

DATE 5/9/97

ANALYST TAN

SIGNATURE John Meyer

TiFeMn - experiment 5 - water extraction

Date Analyzed	Actual Percent DMMP	Determined Percent DMMP	Percent Recovered
05/07/97	1.97%	0.00%	0.00%
05/07/97	1.97%	0.00%	0.00%
05/07/97	1.97%	0.00%	0.00%
05/07/97	1.97%	0.00%	0.00%
05/07/97	1.97%	0.17%	8.47%
05/07/97	1.97%	0.14%	6.89%
05/07/97	1.97%	0.11%	5.43%
05/08/97	1.97%	0.00%	0.00%
05/08/97	1.97%	0.91%	46.35%
05/08/97	1.97%	0.00%	0.00%
05/08/97	1.97%	0.13%	6.40%
05/08/97	1.97%	0.00%	0.00%
05/08/97	1.97%	0.00%	0.00%
05/08/97	1.97%	0.00%	0.00%
05/08/97	1.97%	0.19%	9.41%
05/08/97	1.97%	0.00%	0.00%
05/08/97	1.97%	0.00%	0.00%
05/09/97	1.97%	0.00%	0.00%
05/09/97	1.93%	0.00%	0.00%
05/09/97	1.93%	0.00%	0.00%

ASKIN RESULTS

MAINSTREAM Engineering Corporation

DATE 5/9/97
ANALYST
SIGNATURE

TiFeMn - no treatment - water extraction

Date Analyzed	Actual Percent DMMP	Determined Percent DMMP	Percent Recovered
05/06/97	1.59%	1.30%	81.82%
05/06/97	1.59%	1.22%	76.49%
05/06/97	1.59%	1.01%	63.33%
05/06/97	1.59%	3.04%	190.83%
05/06/97	1.59%	1.54%	96.35%
05/06/97	1.59%	1.67%	104.92%
05/06/97	1.59%	2.70%	169.36%
05/06/97	1.59%	1.63%	102.23%
05/06/97	1.59%	2.28%	143.30%
05/06/97	1.59%	2.37%	148.55%
05/06/97	1.59%	2.78%	174.54%
05/06/97	1.59%	2.43%	152.54%
05/06/97	1.59%	2.37%	148.79%
05/06/97	1.59%	2.31%	144.76%
05/06/97	1.59%	2.34%	147.14%
05/07/97	1.86%	2.51%	135.36%
05/07/97	1.86%	2.36%	127.26%
05/07/97	1.86%	2.74%	147.40%
05/07/97	1.86%	2.79%	150.43%
05/07/97	1.86%	2.67%	143.98%

ASKIN RESULTS - Statistical Summary

MAINSTREAM Engineering Corporation

DATE 5/16/97

ANALYST CA

SIGNATURE

TiFeMn - experiment 5 - water extraction

Anova: Single Factor

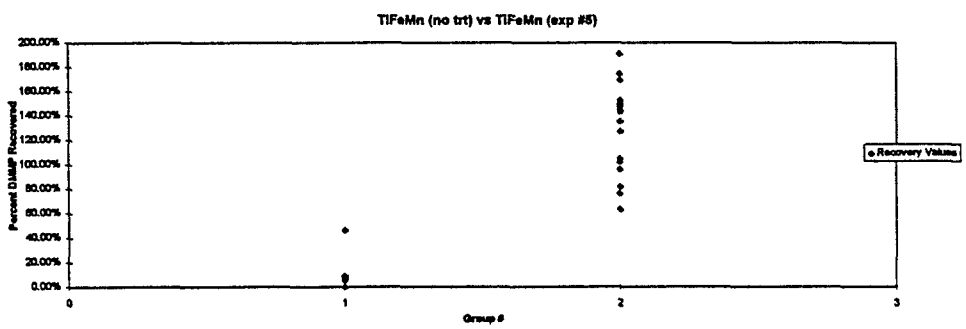
SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
1: TiFeMn - exp #5	20	0.829511811	0.041475591	0.01095993
2: TiFeMn - no trt wat ext	20	26.49371762	1.324685881	0.116414591

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	16.46628649	1	16.46628649	258.549141	1.52559E-18	4.098168915
Within Groups	2.420115899	38	0.063687261			
Total	18.88640239	39				

Conclusion: There is a significant difference (95% probability) between groups



ASKIN RESULTS

MAINSTREAM Engineering Corporation

DATE 5/19/97
ANALYST
SIGNATURE

Mole seive only

Date Analyzed	Actual Percent DMMP	Determined Percent DMMP	Percent Recovered
05/19/97	4.61%	3.27%	71.00%
05/19/97	4.61%	2.59%	56.28%
05/19/97	4.61%	3.38%	73.34%
05/19/97	4.61%	4.58%	99.35%
05/19/97	4.61%	3.66%	79.49%

ASKIN RESULTS

MAINSTREAM Engineering Corporation

DATE 5/19/97

ANALYST DAM

SIGNATURE

Mole sieve with methyl methacrylate monomer added, no hydrogen treatment

Date Analyzed	Actual Percent DMMP	Determined Percent DMMP	Percent Recovered
05/16/97	3.27%	2.90%	88.55%
05/16/97	3.27%	2.14%	65.38%
05/16/97	3.27%	1.31%	40.16%
05/16/97	3.27%	1.84%	56.17%
05/16/97	3.27%	1.55%	47.23%

ASKIN RESULTS - Statistical Summary

MAINSTREAM Engineering Corporation

DATE 5/19/97
ANALYST TMM
SIGNATURE Robert Meyer

Mole sieve with methyl methacrylate monomer added, no hydrogen treatment

Anova: Single Factor

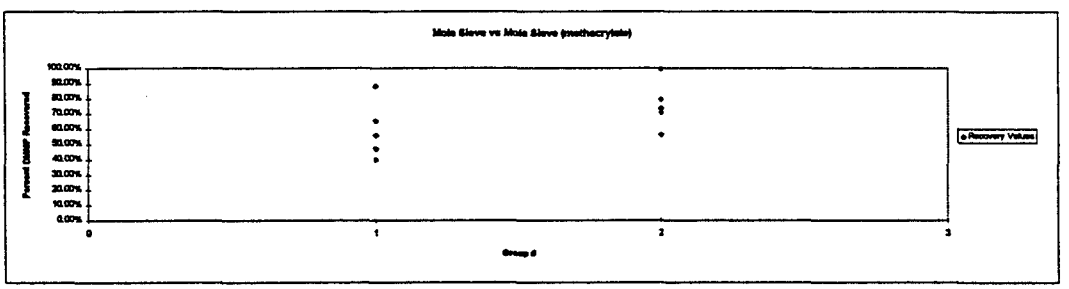
SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
1: Mole sieve	5	2.974899089	0.594979818	0.035358967
2: Mole sieve (methacrylate)	5	3.794594176	0.758918835	0.024464189

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.067190004	1	0.067190004	2.246287498	0.172317436	5.317644991
Within Groups	0.239292623	8	0.029911578			
Total	0.306482627	9				

Conclusion: There is no significant difference (95% probability) between groups



ASKIN RESULTS

MAINSTREAM Engineering Corporation

DATE 5/19/97

ANALYST DAN

SIGNATURE John D Mays

Mole sieve with proplene glycol butyl ether added, no hydrogen treatment

Date Analyzed	Actual Percent DMMP	Determined Percent DMMP	Percent Recovered
05/16/97	2.87%	2.82%	98.35%
05/16/97	2.87%	1.81%	63.20%
05/16/97	2.87%	3.49%	121.90%
05/16/97	2.87%	4.56%	159.28%
05/16/97	2.87%	1.95%	68.10%

ASKIN RESULTS - Statistical Summary

MAINSTREAM Engineering Corporation

DATE 5/19/97

ANALYST TAM

SIGNATURE John Meyer

Mole sieve with proplene glycol butyl ether added, no hydrogen treatment

Anova: Single Factor

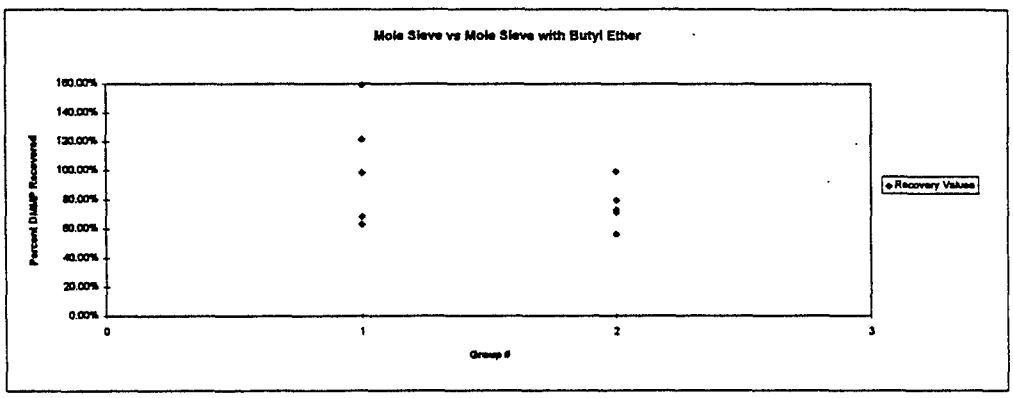
SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
1: Mole Sieve	5	5.108346517	1.021669303	0.158618295
2: Mole sieve (butyl ether)	5	3.794594176	0.758918835	0.024464189

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.172594521	1	0.172594521	1.885429102	0.206970196	5.317644991
Within Groups	0.732329934	8	0.091541242			
Total	0.904924455	9				

Conclusion: There is no significant difference (95% probability) between groups



DEPARTMENT OF THE ARMY
US ARMY MEDICAL RESEARCH AND MATERIEL COMMAND
504 SCOTT STREET
FORT DETRICK, MARYLAND 21702-5012

REPLY TO
ATTENTION OF:

MCMR-RMI-S (70-1y) 4 Dec 02

MEMORANDUM FOR Administrator, Defense Technical Information Center (DTIC-OCA), 8725 John J. Kingman Road, Fort Belvoir, VA 22060-6218

SUBJECT: Request Change in Distribution Statement

1. The U.S. Army Medical Research and Materiel Command has reexamined the need for the limitation assigned to technical reports written for this Command. Request the limited distribution statement for the enclosed accession numbers be changed to "Approved for public release; distribution unlimited." These reports should be released to the National Technical Information Service.

2. Point of contact for this request is Ms. Kristin Morrow at DSN 343-7327 or by e-mail at Kristin.Morrow@det.amedd.army.mil.

FOR THE COMMANDER:

Encl

PHYLIS M. RINEHART
Deputy Chief of Staff for
Information Management

ADB218773
ADB223531
ADB230017
ADB223528
ADB231930
ADB226038
ADB224296
ADB228898
ADB216077
ADB218568
ADB216713
ADB216627
ADB215717
ADB218709
ADB216942
ADB216071
ADB215736
ADB216715
ADB215485
ADB215487
ADB220304
ADB215719
ADB216072
ADB222892
ADB215914
ADB222994
ADB216066
ADB217309
ADB216726
ADB216947
ADB227451
ADB229334
ADB228982
ADB227216
ADB224877
ADB224876
ADB227768
ADB228161
ADB229442
ADB230946
ADB230047
ADB225895
ADB229467
ADB224342
ADB230950
ADB227185
ADB231856
ADB229914
ADB229497
ADB230947
ADB282209
ADB270846
ADB282266
ADB262442
ADB256670