RESEARCH IN THE SYNTHESIS AND CHARACTERIZATION OF MAGNETIC FLUIDS
(PHASE II)

Prepared by

Avco Space Systems Division
Avco Corporation
Lowell, Massachusetts

GPO PRICE $ ________

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ff 653 July 65

AVSSD-0038-68-CR

Quarterly Report No. 3

January 1968 to March 1968

Contract No. NASW-1581

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Prepared for

National Aeronautics and Space Administration
Office of Advanced Research and Technology
Washington, D. C. 20546

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NOTICE

This is the third of a series of quarterly reports under a contract with the National Aeronautics and Space Administration to provide continued research in the synthesis and characterization of magnetically polarizable colloidal fluids.

This program is performed in the Ferrohydrodynamics Section under the leadership of Dr. R. E. Rosensweig. The Principal Scientific Investigator is Dr. R. Kaiser. Mr. J. Zgrebnak also participated in the effort during this quarter.

ABSTRACT

The viscosity of different ferrofluids have been measured in a 500 oe magnetic field. Application of a field results in an increase in viscosity which in one case was as low as 5%. Addition of sulfur chloride to a linseed oil fatty acid stabilized ferrofluid in order to form a polymerized "overshoe" around the individual particles, results in flocculation of the magnetic particles. The effect of solvation on fluid stability is discussed.

Stable water base and fluorocarbon base magnetite ferrofluids have been prepared by grinding. Encouraging results have been obtained in an attempt to prepare a silicon-iron ferrofluid. The effect of surfactant structure and solubility on magnetite/kerosene ferrofluids is discussed.

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A. INTRODUCTION/OVERALL PROGRESS

Some novel ferrofluids have been prepared by the grinding technique. A stable water based magnetic colloid was made with a cationic surfactant, Aerosol C 61. Some long chained fluorinated surfactants were obtained. As a result, it was possible to prepare a fluorocarbon base ferrofluid for the first time. These systems should be of great practical interest since they are immiscible with both oil and water. The first indications that it is possible to prepare a metal base ferrofluid by grinding were observed after 2000 hours in a run in which silicon-iron powder is being ground in the presence of a kerosene/oleic acid mixture. The effects of surfactant structure and solubility were examined by comparing the results obtained by grinding magnetite in kerosene in the presence of fatty amines as compared to other surfactants of similar structure but different end groups. The effect of systematic addition of ethoxy groups to a surfactant family on ferrofluid formation was examined using the Triton series of ethylene oxide adducts of octyl phenol. The effectiveness varied markedly with chain length with a sharp maximum occurring for the adduct containing an average of three ethylene oxide molecules.

The viscosity of a ferrofluid in the presence of a magnetic field was measured for the first time. In some cases, there was less than a 10% change in viscosity at 50% of fluid saturation. Equipment to generate the higher fields needed to saturate the fluids is being obtained in order to be able to make some more extensive parametric measurements.

Addition of a sulfur chloride solution in kerosene to linseed oil fatty acid stabilized ferrofluid resulted in flocculation of the ferrofluid. These results indicate the effect of solvation of the monolayer on the stability of a ferrofluid in critical. The "overshoe" concept for the preparation of more thermally stable ferrofluids can only be feasible if the polymerization ester does not render the adsorbed layer too rigid, as appears to be the case with triply unsaturated linolenic acid - the principal component of linseed oil fatty acid.

B. GRINDING RUNS

The results of the grinding experiments performed during the course of this quarter are summarized in Table I.

1. Water Base Fluids

A ferrofluid was formed by grinding magnetite in water in the presence of Aerosol C-61 (G104) a monomeric cationic surfactant manufactured by American Cyanamid. The material was allowed to stand undisturbed for 10 weeks after the end of the grinding run prior to processing to insure that the colloid was stable. The material did not flocculate in this period of time as did the polymeric dispersants used before (Tamol 731). This ferrofluid is now being processed further (centrifugation and concentration) and characterized.

A number of attempts were also made to prepare a water base ferrofluid by grinding in the presence of a number of non-ionic surfactants (G109, G114). These runs were discontinued because of severe foam formation in the mills. If a low foaming non-ionic surfactant with good dispersing properties can be found, an attempt will be made to prepare a water base ferrofluid with this material. The reasons for such an experiment are:

1. Determination of the relative importance of various stabilization mechanisms in water ionic repulsion (double layer) as compared to solvation.
2. There are possibilities that an ionic double layer might be thicker than a solvated layer so that a higher magnetite concentration could be attained in the later case - leading to magnetically more responsive ferrofluids.

2. Grinding of Metals

At the start of the quarter, there were continued difficulties in obtaining a metal-base ferrofluids by the grinding technique that has successfully resulted in magnetite base ferrofluids. As reported in the last progress report, none of the attempts at preparing a metal base ferrofluid had proved to be successful (Runs G83, G84, G94, G100, and G102).

Dispersion tests were performed on various metal powders to determine whether the choice of a surfactant that was successful with magnetite would be suitable with a metal. Similar screening tests had been previously run with magnetite. It had been presumed that the adsorption characteristics of the metal and metal oxide would be similar. These dispersion tests were run with Carbonyl Iron Powder W (General Aniline & Film Co), Carbonyl Iron Powder SF (General Aniline & Film Co) and with Lodex Round Cobalt-iron (General Electric Co); in kerosene in the presence of different surfactants, as shown in Table II. Some of the surfactants tried had a definite effect on the settling rate of the iron powders used, the Iron SF powder being more affected then the the Iron W powder. With both these materials, the ethylene oxide adducts of long chain alcohols proved to be good dispersants. Other materials which are good

TABLE I

TABULATION OF GRINDING RUNS

Key to Comments:

I.	Successful ferrofluid formed with initial mixture of intredients
II.	Successful ferrofluid formed with the addition of extra carrier liquid to break transient gel formation
III.	Successful ferrofluid formed with the addition of extra surfactant to break transient gel formation
IV.	Successful ferrofluid formed with the addition of extra surfactant and carrier fluid to break transient gel formation
V.	Unsuccessful run, initial colloid formation followed by formation of intractable gel
VI.	Unsuccessful run, no initial colloid formation
VII.	Unsuccessful run, initial colloid formation followed by flocculation
A.	Strong fluid formed, $M_s > 150$ gauss
B.	Medium fluid formed, $75 < M_s < 150$ gauss
C.	Weak fluid formed, $M_s < 75$ gauss

Standard Composition of Charges:

Ball Mill Capacity	Carrier Liquid, cc	Surfactant cc	Magnetic Powder cc
2.0 pint	300	20	10
4.7 pint	625	50	20
1.6 gal/2.0 gal	1250	100	40
3.0 gal	3750	300	120

TABLE I

Charge	Carrier Fluid	Dispersant	Dispersant Formula	Magnetic Powder	Time (Hrs.)	Comments
G-94 4.7 pt.	Kerosene	Oleic acid	$CH_3-(CH_2)_7CH=CH(CH_2)_7COOH$	Silicon Iron (14% Silicon)	3495	In progress
G-95 1.6 gal	Water	Tamol 731	Sodium Salt of a Poly-carboxylic acid	Magnetite $FeO.Fe_2O_3$	70	Gasket Failure Lost Sample
G-96 1.6 gal	Kerosene	ENJAY 3854	High Temperature Polymeric Oil Soluble Dispersant	Magnetite $FeO.Fe_2O_3$	439	IA
G-97 1.6 gal	Water	Tamol 731	See G-95	Magnetite $FeO.Fe_2O_3$	981	IA 1.5cc Surfactant/ grams solids
G-98 4.7 pt.	Kerosene	Oleic acid	$CH_2-(CH_2)_7CH=CH(CH_2)_7COOH$	Magnetite $FeO.Fe_2O_3$	1736	IIB Tungsten Carbide balls
G-99 1.6 gal	Kerosene	Aerosol OT (American Cyanamide)	$CH_2-\ COOC_6H_{13}$ $CH_2-\ COOC_6H_{13}$ SO_3Na	Magnetite $FeO.Fe_2O_3$	2967	IVC
G-100 1.6 gal	Kerosene	Santolube 393 (Monsanto Chemical Co.)	Zinc Sulfophosphate Oil additive	Carbonyl Iron W (General Aniline Film Co.)	2493	VI
G-101 1.6 gal	Kerosene	ENJAY 3854	See G-96	Magnetite $FeO.Fe_2O_3$	583	IA

TABLE I Cont'd

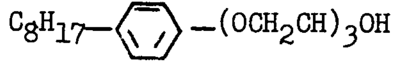
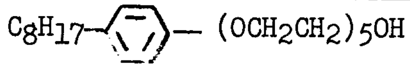
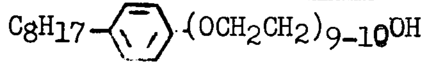
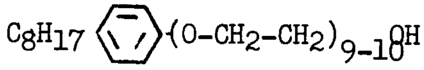
Charge	Carrier Fluid	Dispersant	Dispersant Formula	Magnetic Powder	Time (Hrs.)	Comments
G-102	Kerosene	ENJAY 3854	See G-96	Lodex Round Cobalt-Iron	1327	VI
G-103 1.6 gal	Kerosene	Oleyl Alcohol	CH_3-(CH_2) CH=$CH(CH_2)_7CH_2OH$	Magnetite $FeO.Fe_2O_3$	2702	In progress
G-104 1.6 gal	Water	Aerosol C 61 (American Cyanamide)	Ethanolated Alkyl Guanidineamine complex	Magnetite $FeO.\ Fe_2O_3$	837	IA
G-105 1.6 gal	Kerosene	Triton X-35 (Rohm & Haas)		Magnetite $FeO.Fe_2O_3$	1480	IA
G-106 1.6 gal	Kerosene	Triton X-45 (Rohm & Haas)		Magnetite $FeO.Fe_2O_3$	1412	IB
G-107 1.6 gal	Kerosene	Triton X-100 (Rohm & Haas)		Magnetite $FeO.Fe_2O_3$	372	VI
G-108 2.0 pt.	Fluorolube FS	Perfluoro Octanoic acid	$CF_3(CF_2)_6$- $COOH$	Magnetite $FeO.Fe_2O_3$	504	VI
G-109 2.0 pt.	Water	Triton X-100 (Rohm & Haas)		Magnetite $FeO.Fe_2O_3$	100	VI (Foam)

TABLE I Cont'd

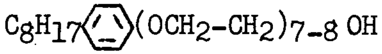
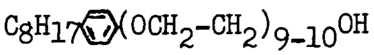
Charge	Carrier Fluid	Dispersant	Dispersant Formula	Magnetic Powder	Time (Hrs.)	Comments
G-110 2.0 pt.	Perfluoro-tributyl-amine	Perfluoro octanoicacid	$CF_3-(CH_2)_6-COOH$	Magnetite $FeO.Fe_2O_3$	768	VI
G-111 1.6 gal	Kerosene	Triton X-15 (Rohm & Haas)		Magnetite $FeO.Fe_2O_3$	1074	In progress
G-112 1.6 gal	Kerosene	Triton X-114 (Rohm & Haas)		Magnetite $FeO.Fe_2O_3$	1079	In progress
G-113 4.7 pt.	Kerosene	Oleylamine	$CH_3-(CH_2)_7-CH=CH-(CH_2)_8-NH_2$	Magnetite $FeO.Fe_2O_3$	1208	IC
G-114 1.6 gal	Water	Neodol 25-7 (Shell Chem. Co.)	$CH_3-(CH_2)_{11-14}-(O-CH_2-CH_2)_7OH$	Magnetite $FeO.Fe_2O_3$	50	VI (Foam)
G-115			O P E N			
G-116 1.6 gal	Kerosene	Triton X-100 (Rohm & Haas)		Magnetite $FeO.Fe_2O_3$	324	VI

TABLE I Concl'd

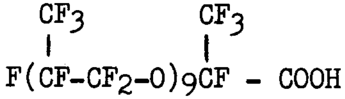
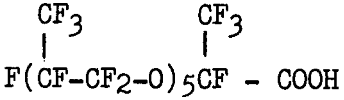
Charge	Carrier Fluid	Dispersant	Dispersant Formula	Magnetic Powder	Time (Hrs.)	Comments
G-117 4.7 pt.	Kerosene	Triton X-45 (Rohm & Haas)	C_8H_{17}⌬$(OCH_2CH_2)_5OH$	Carbonyl Iron Powder SF (General Aniline Film)	324	In progress
G-118 2.0 pt.	Freon E3 Fluorinated Ether	Hexafluoro propylene epoxide hexamer acid	 $F(\overset{CF_3}{\overset{\vert}{CF}}-CF_2-O)_9\overset{CF_3}{\overset{\vert}{CF}} - COOH$	Magnetite $FeO.Fe_2O_3$	324	In progress
G-119 2.0 pt.	Freon E3 Fluorinated Ether	Hexafluoro propylene epoxide decamer acid	 $F(\overset{CF_3}{\overset{\vert}{CF}}-CF_2-O)_5\overset{CF_3}{\overset{\vert}{CF}} - COOH$	Magnetite $FeO.Fe_2O_3$	324	In progress
G-120 1.6 gal	Kerosene	Linoleic acid	$CH_3-(CH_2)_4-(CH=CH-CH_2)_2-(CH_2)_6-COOH$	Magnetite $FeO.Fe_2O_3$		In progress

Table II

Dispersion Tests of Metal Powders in Kerosene

Surfactant	Settling Time Minutes Carbonyl Iron W	Carbonyl Iron SF	Lodex Round
Triton X 100	21	over 600	No suspension
Triton X 45	17	34	No suspension
Neodol 25-7 (Shell Oil Co.)	17	40	No suspension
Triton X 114	14	55	
Oleic Acid	14	over 600	No suspension
Oleyl Amine	12		
Triton X 35	12		
Triton X 15	11		
UCC L-78 Silicone Surfactant	11		
UCC L-77 Silicone Surfactant	10		
UCC L-75 Silicone Surfactant	10		
Oleyl Alcohol	9		
Tenlo 70	7	16	
Lecithin	7		
Aerosol OT	7		
Zinc Naphthanate	6		
Aluminum Naphthanate	6		
Santolube 393 (Monsanto Chem. Co).	6		
Santopoid Monsanto Chem. Co.)	6		
Enjay 3854 (Humble Oil Co.)	6		
Enjay 3029 (Humble Oil Co.)	6		
Blank	6	7	No suspension

magnetite dispersants such as Tenlo 70 and Enjay 3854, proved to be poor dispersants for these iron powders.

None of the surfactants tried had any effect on the settling rate of Lodex particles in kerosene. In all cases, the Lodex powder settled as coarse agglomerates that were visible to the eye.

One major difference between the two grades of iron powder and the Lodex powder used is the size of the particles. The iron particles are in the range of 2-4 microns in diameter while the Lodex particles are in the 500 Å range, approximately two orders of magnitude smaller in size. With these smaller particles, the ratio of the attractive forces bonding the particles together to their weight is so high that the agglomerated powder was unaffected by the mild disruptive forces introduced by the agitation of the suspension, in spite of the presence of the surfactants.

The various runs in which a metal powder was being ground in the presence of a surfactant that failed the dispersion test were stopped (G100, G102). The failure of these runs to produce a satisfactory ferrofluid was considered due to a poor choice of surfactant.

One run (G 94) in which a metal powder was being ground in kerosene, in the presence of oleic acid, was continued on the basis of these dispersion tests in spite of the fact that very poor results had been obtained after 2000 hrs. of grinding.

A significant increase in ferrofluid density and saturation magnetization was observed for the first time 2300 hours of grinding time. Further increases in density and magnetization with further grinding time, up to 3500 hours, have since been observed. The magnetization and density of samples that were spun in a laboratory centrifuge for 10 minutes and 1 hour respectively are presented in Figures 1 and 2. Assuming a nominal acceleration of 2000 gee, the limiting sizes of the particles remaining in suspension in these two cases are 2100 Å and 840 Å respectively. Based on the initial composition of the feed, which contained 2.9% silicon (14%) - iron powder (M_s = 15000 gauss ρ = 7.2 gr/cc) the density and magnetization measurements indicate that over 90% of the initial powder had been reduced to a particle size of less than 2100 Å, but that less than 10-20% has been reduced to below 840 Å. With the smaller particle size, the magnetization measurements yield a lower value which might be due to partial oxidation of these particles, which could be due to either an error in the measurement or to partial oxidation of the particles in suspension.

These results indicate that it is possible to grind a metal powder in the presence of a surfactant. The initial powder was a nominal -200 mesh material (74 micron). There has been an over three hundred fold reduction in particle size. The process, however, is very slow.

Another run was started with a metal powder (G 117). The iron powder in this case has a smaller initial particle size (2μ - 4μ). The surfactant

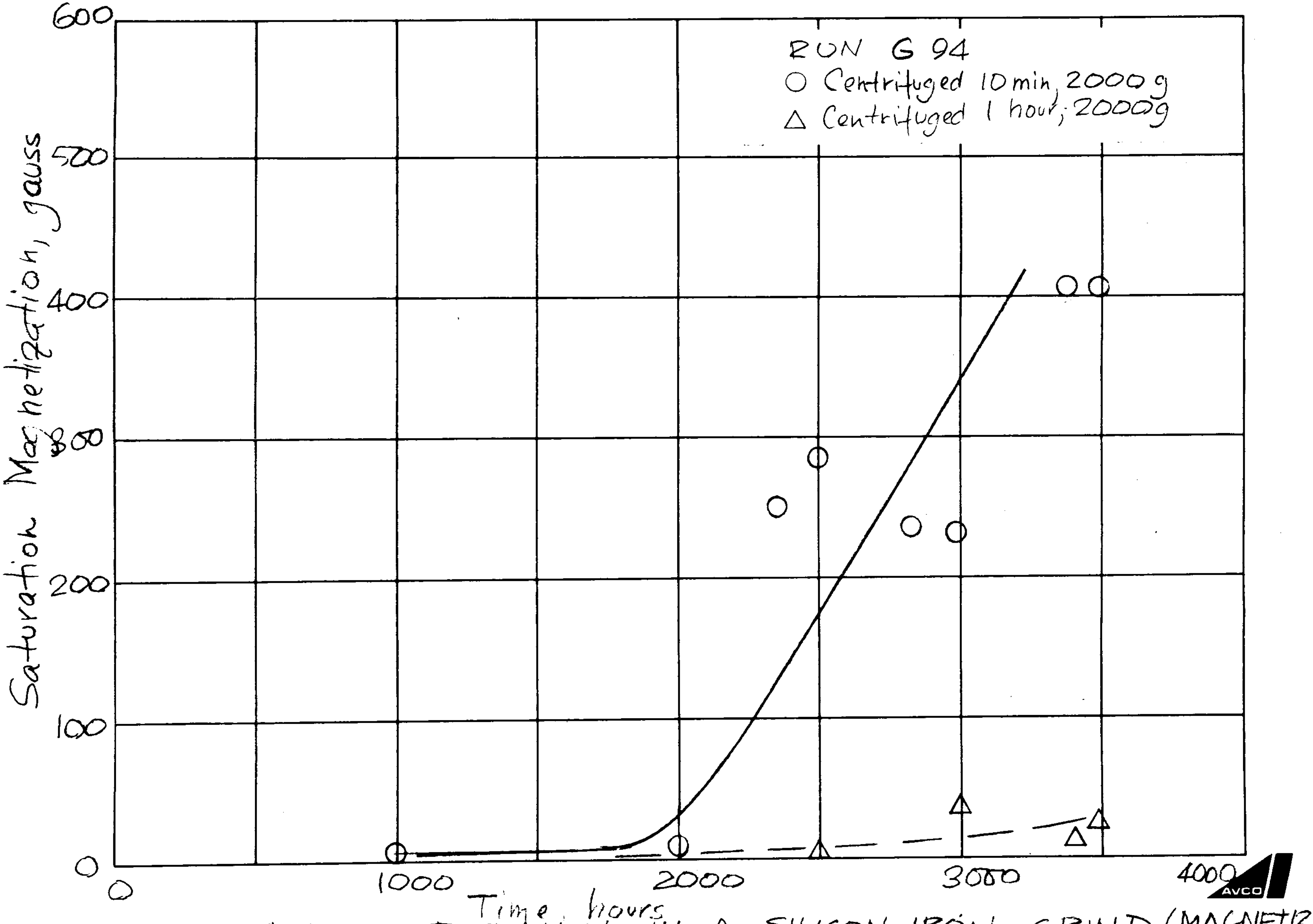


Figure 1 COLLOID FORMATION IN A SILICON-IRON GRIND (MAGNETIZATION)

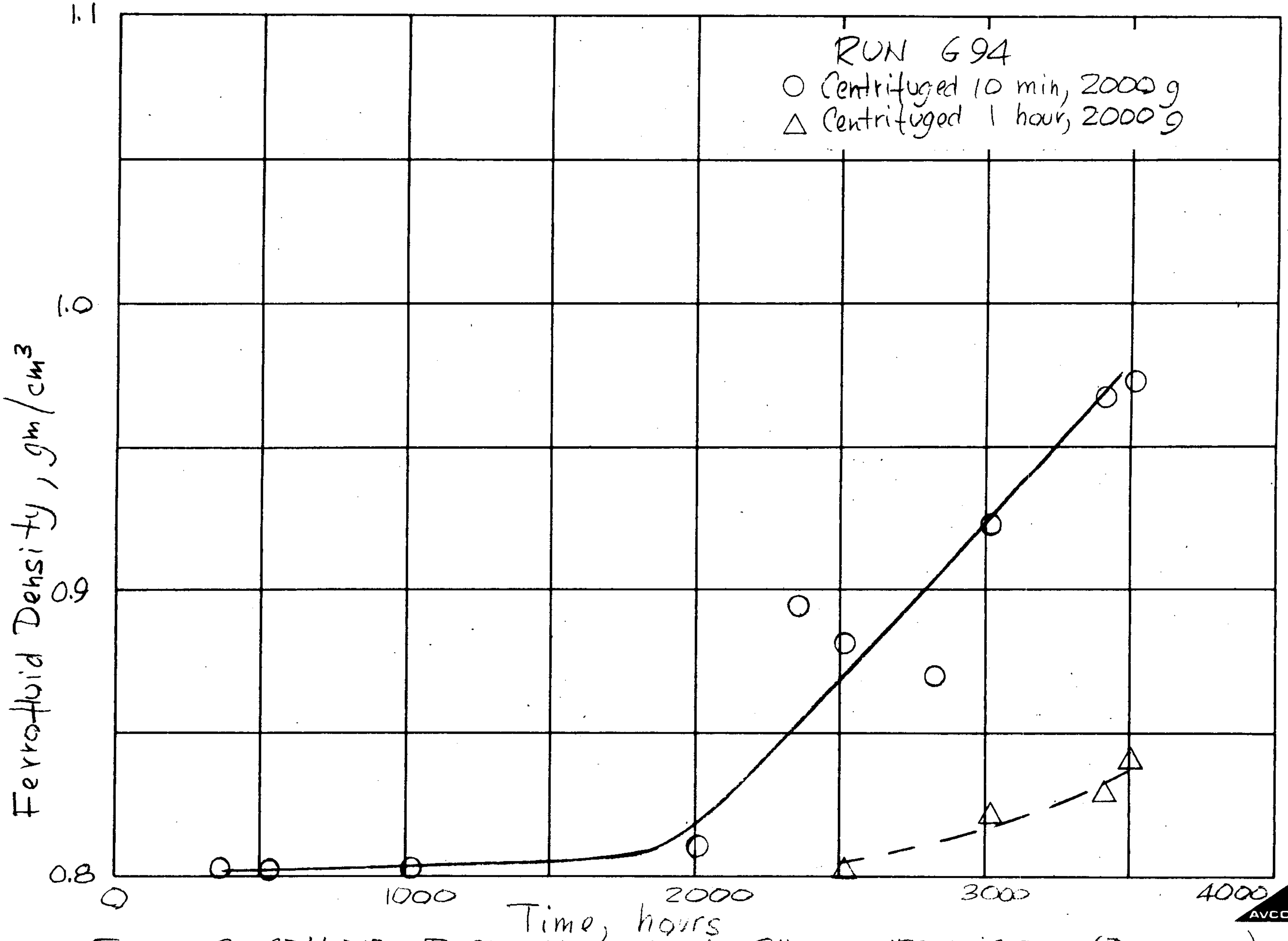


Figure 2. COLLOID FORMATION IN A SILICON-IRON GRIND (DENSITY)

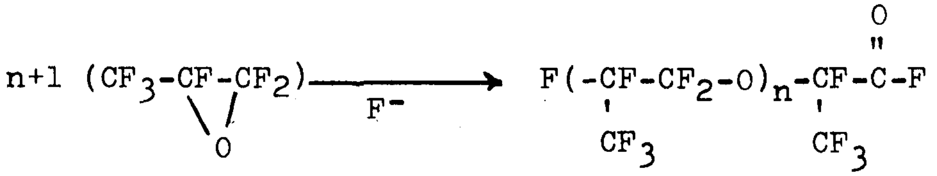
used was found to be an effective dispersant. The alcohol terminal group is less reactive than the carboxylic group of oleic acid. This grade of carbonyl is considered hard and brittle, as is silicon iron. A faster rate of colloid formation is therefore expected in this run.

3. Fluorocarbon Base Fluids

The fluorocarbons are an unusually inert and stable family of compounds (viz., Teflon). They have found wide application in many areas because of these properties. The fluorocarbon liquids in particular have the characteristic that they are immiscible with both oil and water systems. This makes them unique carriers for ferrofluids. It was decided to attempt to prepare such fluorocarbon base fluids. This study is of fundamental interest as well since little is known about the preparation and characterization of colloid systems in these very inert liquids.

The first runs were made with the longest perfluorinated surfactant that is commercially available, perfluoro-octanoic acid (G 108 and G 110). These runs were made in small mills because of the high cost of these fluorinated materials. In both cases there was no colloid formation whatsoever. The reason for the failure of these runs is believed due to the fact that perfluoro-octanoic acid was too short a molecule. By comparison in hydrocarbon systems grinding of magnetite in kerosene does not result in colloid formation in the presence of octanoic acid. All surfactants shorter than twelve carbon atoms in length have failed to produce a colloid in hydrocarbon systems. It was presumed that the same would be true of fluorocarbon systems.

After extensive inquiries, it was found that Dr. P.L. Bartlett of the Experimental Station of E.I. DuPont de Nemours & Co. was developing some long chain fluorocarbon surfactants. These surfactants are prepared by the anionic polymerization of hexafluoropropylene oxide (HFPO) at low temperatures which yields perfluoropolyethers that have an acyl fluoride end group.



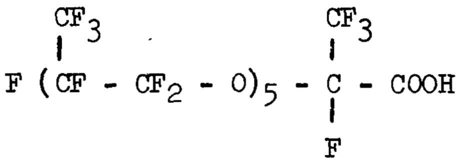
$$n{+}1\ (\underset{\diagdown\,O\,\diagup}{CF_3\text{-}CF\text{-}CF_2}) \xrightarrow[F^-]{} F(-\underset{CF_3}{CF}\text{-}CF_2\text{-}O)_n\text{-}\underset{CF_3}{CF}\text{-}\overset{\overset{O}{\|}}{C}\text{-}F$$

The acyl end group is then hydrolyzed to yield a carboxylic terminal group. By controlling the degree of polymerization, any desired chain length can be obtained.

The reactive end group can also be stabilized by a number of techniques which result in the substitution of hydrogen or fluorine for the carboxyl group. The stabilized perfluoropolyethers which result are very inert liquids. They are marketed by DuPont as the Freon E Series of fluorocarbon liquids.

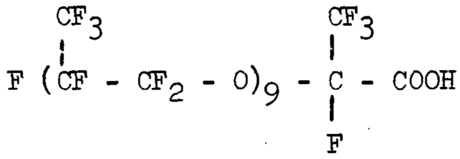
Through the courtesy of Dr. Bartlett, experimental quantities of the following fluorocarbon surfactants were obtained:

1. HFPO Hexamer Acid



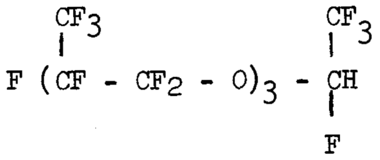
$F(\overset{CF_3}{CF} - CF_2 - O)_5 - \underset{F}{\overset{CF_3}{C}} - COOH$

2. HFPO Decamer Acid



$F(\overset{CF_3}{CF} - CF_2 - O)_9 - \underset{F}{\overset{CF_3}{C}} - COOH$

An additional amount of Freon E3 fluorinated ether was also provided:



$F(\overset{CF_3}{CF} - CF_2 - O)_3 - \underset{F}{\overset{CF_3}{CH}}$

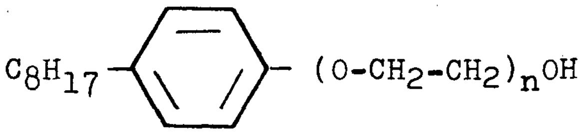
Two magnetite grinding runs were initiated with Freon E3 as the carrier liquid using HFPO hexamer acid and HFPO decamer acid as the stabilizing agents (G 118 and G 119). In both cases, there was positive evidence of colloid formation. After 324 hrs. of grinding, the saturation magnetization of the ferrofluids were 18 gauss (G 118) and 28 gauss (G 119). These rates of colloid formation are comparable to those obtained by grinding magnetite in oleic acid/kerosene systems.

These runs will be allowed to grind to completion, barring unforeseen complications. The properties of these ferrofluids should prove to be most interesting.

4. Kerosene/Magnetite System

a. Hydroxyl Terminated Surfactants

A series of runs were carried out with different hydroxyl terminated surfactants. These included oleyl alcohol (G 103) and a series of ethylene oxide adducts of octyl-phenol in which the number of ethylene oxide units was systematically varied between one and ten (G105, G106, G107, G111, G112, and G116). These surfactants had the following general formula



These surfactants are sold by Rohm and Haas under the Triton Trademark.

Some very interesting results were obtained which can be summarized as follows:

1. With all the Triton surfactants, except X-100, the amount of colloid formed increased with time and then leveled off. There was no gel formation. With X-100, there was no colloid formation.

2. For a given volumetric concentration of surfactant, the greatest amount of magnetite was incorporated with Triton X 35 ($n = 3$). The ferrofluid resulting from grind G 106 had a saturation magnetization of 172 gauss, and a density of 0.934 gr/cc. The corresponding values of volumetric concentration of magnetite in suspension are 3.04% and 3.12%. This indicates that all the magnetite originally added to the mill was ground to colloidal dimensions with little contamination.

3. The amount of magnetite that was ground decreased as the number of ethylene oxide units in the molecule increased above the value of 3. With $n = 5$ (X 45, G 106), the saturation magnetization of the liquid decreases to 132 gauss; with $n = 7$-8 (X 114, G 112), it decreases to about 80 gauss and with $n = 9$-10 (X 100, G 107, G 116) there is no colloid formation, as previously mentioned.

4. The shortest chain surfactant of the series, X 15, (G 111) was not an effective grinding agent. After 1000 hours of grind the magnetization had only reached a value of 10 gauss which is negligible in comparison to the value achieved by using X 35 as a grinding aid.

These results were interpreted as follows: 1) Triton X 15 is not an effective grinding agent because the surfactant molecule is too short to provide a sufficient stabilizing layer. The principal component of this product is $C_8 H_{17}$-⌬ — $O - CH_2 - CH_2 - OH$ which is approximately 15 Å units long on a molecular scale (C_8H_{17} = 8 Å, ⌬ = 3 Å, $- O - CH_2 - CH_2 - OH$ = 4 Å). Triton X 35 has three ethylene oxide units which increases the length of the molecules to about 21 Å. The slight amount of magnetization is due to the Triton products which are not pure monomolecular species, so that Triton X 15 contains some longer chained species than the monomolecular product. Comparison of the results obtained with X 15 and X 35 establishes that the limiting value on the length of surfactant to be used has to be greater than 15 Å but less than 21 Å. This is in agreement with previous results obtained that the surfactant that was about 12 Å in length (undecanoic acid) was not satisfactory but that one that was 20 Å in length (oleic acid) was. 2) Surfactants of increasing chain length above X 35 become decreasingly less effective on an equal volume basis, because the solubility characteristics of the Triton surfactants change with the number of ethylene oxide units present. Triton X 15 and Triton X 35 are both soluble in aliphatic hydrocarbons such as kerosene at any concentration level. (Triton X 45 is much less soluble). Triton X 45 is soluble at high concentrations (above 10-15%), which is in the range of interest of the present grinding studies. This is explained by the fact that Triton X 45 is a mixture with respect to polyoxyethylene chain length with five oxyethylene units predominating. The longer polyoxyethylene chain members present are insoluble in refined paraffic solvents and only at high concentrations of Triton X 45 is there present a sufficient concentration of the short chain members to solubilize completely the long chain members.

This situation becomes increasingly more pronounced with Triton X-114 and X-100 where the average chain lengths increase and the concentration of smaller chain components which act as coupling agents decreases. With X 100 in fact there is no solubility whatsoever and no colloid formation.

Some preliminary experiments with the ferrofluid produced with grind G 106 (Triton X 45) indicates that this material differs in its compatibility characteristics from the ferrofluids prepared with more oleophilic surfactants such as Tenlo 70, oleic acid, Triton X 35. All attempts to transfer the kerosene base ferrofluids prepared with the last name surfactants to more polar carrier liquids failed because the colloid flocculated. The ferrofluid prepared with Triton X 45 in kerosene has proved to be compatible with liquids of intermediate polarity such as esters. This finding will be investigated further. This is an important result from a practical point of view. Since many esters combine many of the properties that are needed for a ferrofluid carrier - low volatility, low viscosity, inertness, wide temperature limits.

b. Amine Terminated Surfactants

Reference is made to the discussions on amines and of surfactant structures presented in the First Quarterly Report. Run G 113 in which oleyl amine was used as a surfactant did not result in a satisfactory grind after 921 hours, the magnetization of the surfactant liquid had leveled off at a value of 23 gauss. These results are similar to the ones obtained with all the other amine surfactants studied to date. These are unexpected findings since fatty amines normally adsorb quite strongly on polar surfaces such as iron oxides. The amines proved to be good dispersing agents in the sedimentation tests. The lipophile structure of some of the amines studied was identical to that of surfactants that had different terminal groups and were effective grinding agents (viz., oleyl amine versus oleic acid or oleyl alcohol).

One possible explanation for these results is that grinding of the magnetite occurs because of the presence and propagation of flaws in its structure. The amines, upon adsorption, are mechanically passive whereas other adsorbed groups which result in grinding such as hydroxyl and carboxyl groups, interact with the surface to form cracks and similar flaws which weaken the particles and lead to further subdivision.

C. VISCOSITY OF FERROFLUIDS IN A UNIFORM MAGNETIC FIELD

The novelty of the ferrofluids developed by Avco is that they retain their liquid characteristics in the presence of an applied magnetic field. This is an easily observable phenomenon; for example, it is possible to stir a ferrofluid in the presence or absence of an applied field. However, a quantitative measurement of fluid viscosity in the presence of a magnetic field is not so easily obtained, for example with a capillary tube viscometer, since field inhomogeneities result in a fluid acceleration or resistance to flow due to the presence of free surfaces. The fluid and the viscosity measuring device have to be immersed in a uniform magnetic field in order to obtain significant measurements.

Equipment

It was possible to obtain measurements of the viscosity of a magnetic fluid in the presence of a magnetic field by placing a Wells-Brookfield viscosimeter in gap of two air coils as shown in Figure 3 .

The standard Wells-Brookfield viscosimeter was described in previous progress reports. The instrument used varied from the standard in that all ferromagnetically responsive parts were replaced with non-magnetic parts with the exception of the cup which had a 2 mil Rhodium-Nickel coating to prevent corrosion. This was found not to interfere with the measurements.

The dimensions of the coils and gap were as follows:

Outer Diameter	10.5 inches
Inner Diameter	5.5 inches
Thickness	3.0 inches
Coil Separation	3.0 inches

A Harvey-Wells D.C. power supply was used in conjunction with the coils. The field in the space occupied by the viscosimeter head was measured by a Bell Hall effect gauss meter and was found to be uniform to at least 2.5 %. The field generated was proportional to the current (32.6 oe/amp). While the power supply used is capable of providing 50 amps (1600 oe) because of severe coil overheating the measurements were mainly made at 15.3 amps (500 oe). One isolated measurement was made at 30 amps (980 oe). In these measurements the fluid is sheared between a rotating cone and plate in the horizontal direction while the magnetic field is applied in a vertical direction. The fluid is totally enclosed in the cup of the viscosimeter and there is no overall displacement of the fluid with respect to the field.

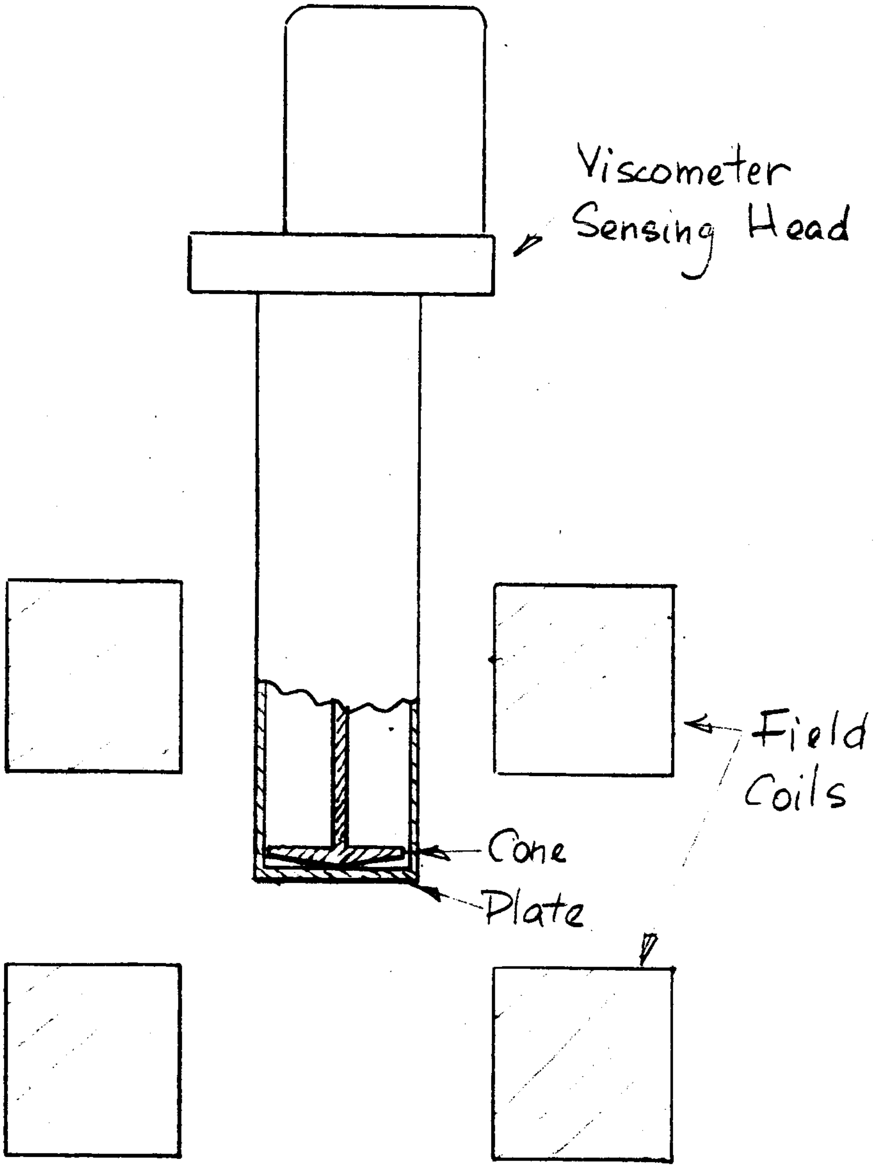


Figure 3 SCHEMATIC OF EXPERIMENTAL ARRANGEMENT TO MEASURE VISCOSITY IN A MAGNETIC FIELD

Results

Preliminary viscosity measurements were made with non-magnetic reference liquids at various shear rates, in the absence of an applied magnetic field and in a 500 oe field. There was no change in measured viscosity as reported in Table III.

Table III

Effect of Magnetic Field on the Viscosity of Non-Magnetic Liquids

Fluid	Temperature °C	Shear Rate sec^{-1}	Viscosity, cp, under Applied Magnetic Field 0 oe	Viscosity, cp, under Applied Magnetic Field 500 oe
Water	20	230	1.4	1.4
		115	1.2	1.3
Dimethyl Silicone Fluid (Dow Corning) DC 200-10	20	115	12.0	11.9
		46	11.8	11.8
		23	11.7	11.6
Dimethyl Silicone Fluid (Union Carbide Corp) L45-50	20	23	63.6	63.8
		11.5	63.8	63.6

The viscosity of five different ferrofluids were measured in the absence of a magnetic field and in a 500 oe field. These results are reported in Table IV and Figures 4 to 7. In one case (1030) the viscosity was also measured in a 1000 oe field. The principal physical properties of these fluids are listed in Table V. Fluids 1020, 1028, and 1032 were discussed in the previous quarterly report, all come from the same basic grind (G 77). They differ, however, in the concentration of magnetic colloid, the average size of these particles, and the viscosity of the base solvent. G 80B is a dilute water fluid whose properties were also presented in a previous quarterly. Fluid 1030 is essentially a standard oleic acid/magnetite ferrofluid.

All the fluids tested experience some increase in viscosity in the presence of a magnetic field. Some of the fluids become non-newtonian as well.

Fluid 1030 exhibits the best change in viscosity. At 975 oe there is less than a 10% change in viscosity. The fluid is at 50% of saturation in this field. At 500 oe, there is only a 5% change in viscosity which remains shear rate independent.

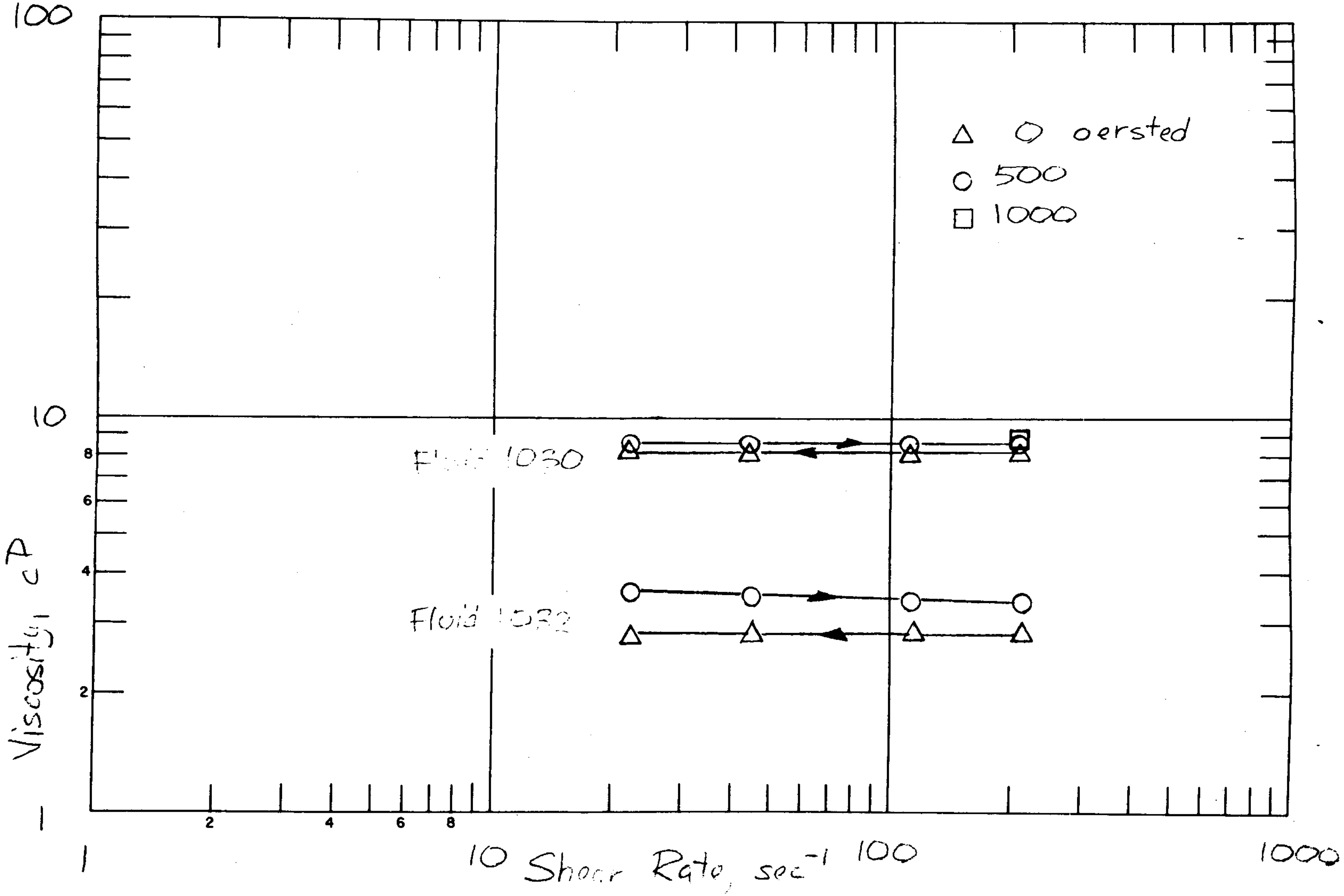


Figure 4 VISCOSITY OF FLUIDS IN A MAGNETIC FIELD

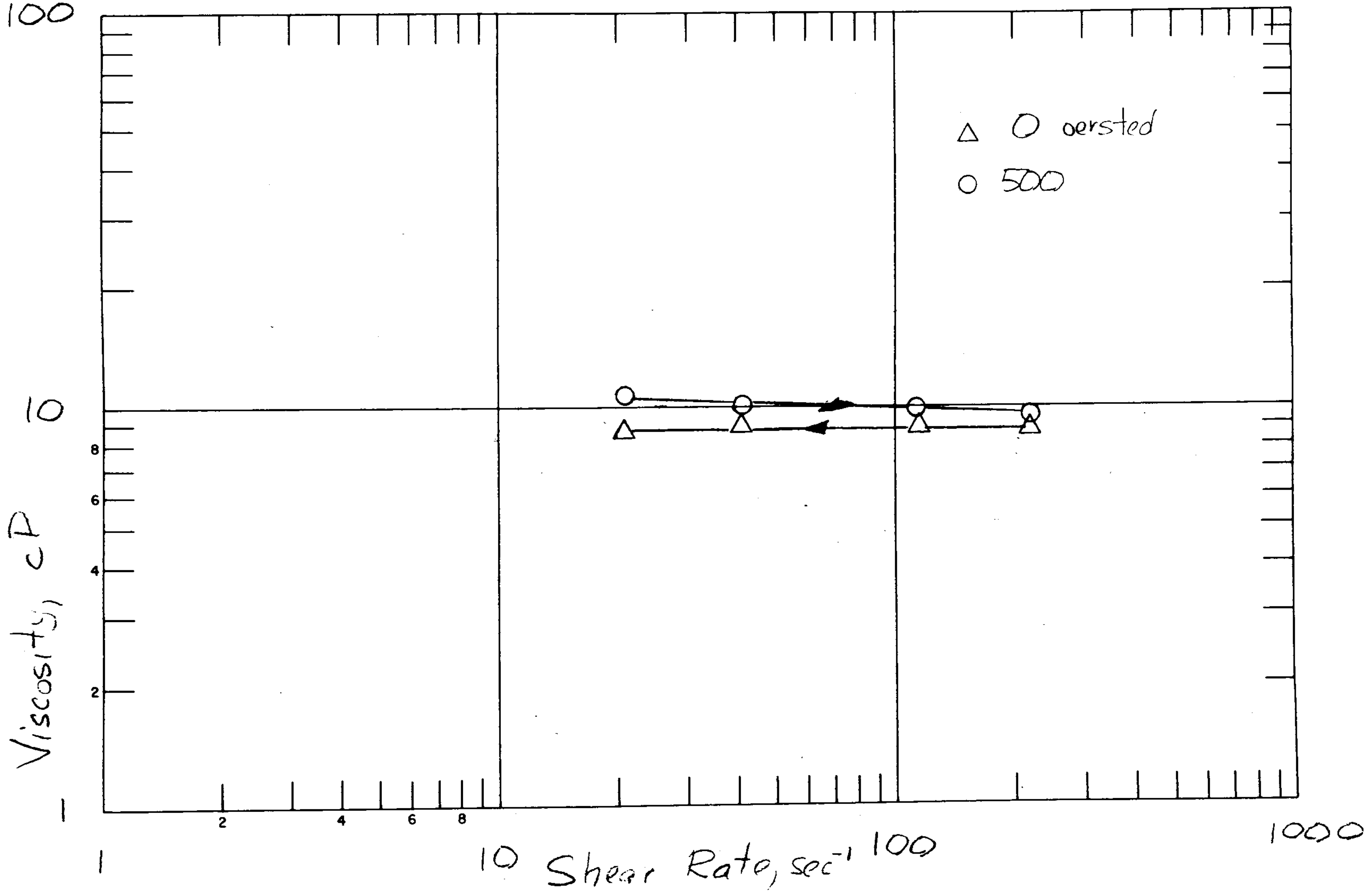


Figure 5 VISCOSITY OF FLUID 1015 IN A MAGNETIC FIELD

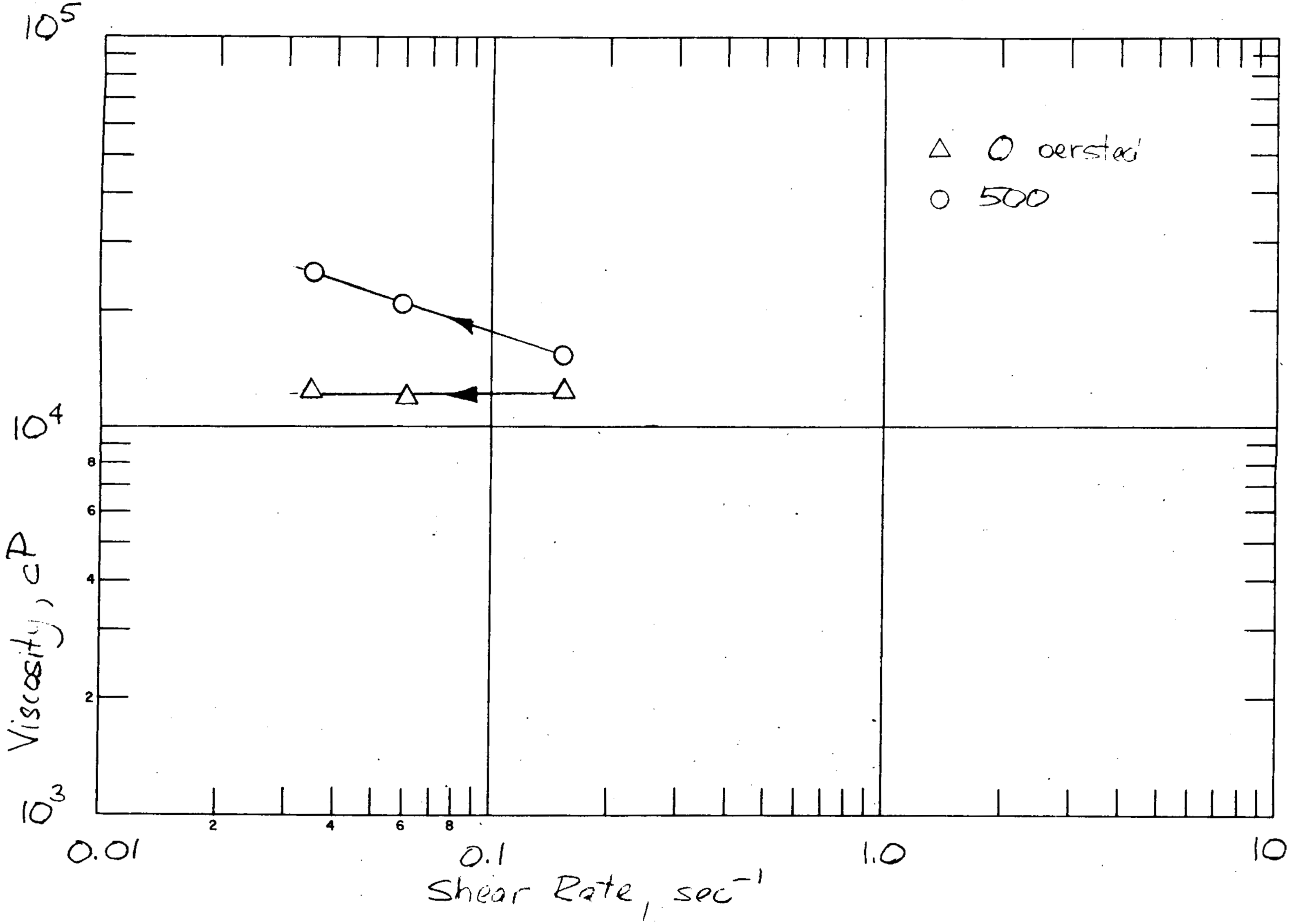


Figure 6 VISCOSITY OF FLUID 102[illegible] IN A MAGNETIC FIELD

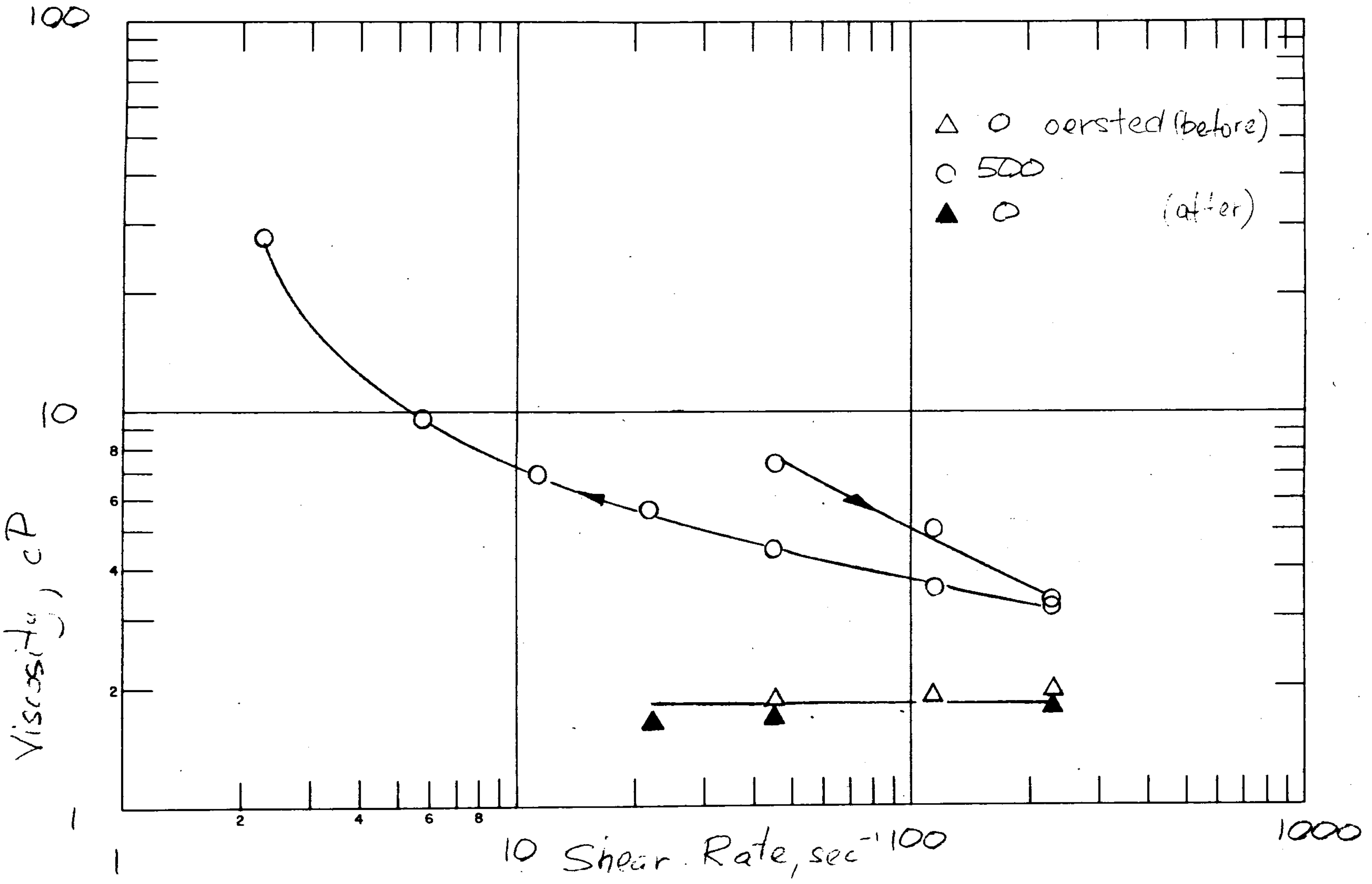


Figure 7 VISCOSITY OF FLUID G80B IN A MAGNETIC FIELD

Fluid 1015 exhibits a 10% - 15% increase in viscosity in a 500 oe field, the viscosity being higher at lower shear rates. This fluid is 50% saturated at this field level.

Fluid 1028, which contains the same magnetic colloid as 1015, but at a higher concentration and in a more viscous base solvent experiences an increase in viscosity which is highly shear rate dependent. Fluid 1032 is a dilute suspension of particles that are larger than those in 1015, which experiences a 20% increase in viscosity which is slightly shear rate dependent. This fluid is about 60% saturated at 500 oe.

The most marked effects were noted with G 80B, a dilute water base liquid. This fluid is 70% saturated in a 500 oe field. This fluid came from a water/Tamol 731 grind of magnetite of what proved to be limited stability.

The viscosity of this fluid in a magnetic field was found to depend on the shear rate and the previous mechanical history of the sample as evidenced by Figure . In the absence of a magnetic force effects disappeared and the liquid was newtonian.

In all the above experiments, there were no residual effects due to the application of a magnetic field.

These measurements can be compared to the effect of a magnetic field on the viscosity of a coarse suspension of magnetizable particles as were used in the Rabinows magnetic clutch. Voet and Suriani(1) measured the viscosity of a 4% by volume suspension of 3 micron iron spheres in a mineral oil/oleic acid dimer mixture. In the absence of a magnetic field, at 30°C, the suspension had a viscosity of 1200 cp over a shear rate range of 0.003 sec^{-1} to 0.03 sec^{-1}. In the presence of a magnetic field produced by a small Alnico magnet, the liquid did not flow until a yield force of 6.8×10^4 dynes/cm^2 was applied.

The increase in viscosity of a suspension of the superperamagnetic particles in the presence of a magnetic field is due to an interaction of aligned particles. There will be an added resistance to flow due to the making and breaking of particle to particle bonds. The magnetic energy between two particles is expressed by the following equation:

$$E_m = - \frac{2\gamma^2}{R^3} = - \frac{M_s^2 \, d^6}{288 \, R^3}$$

Table IV

Effect of Magnetic Field on the Viscosity of Ferrofluids

Ferrofluid No.	Magnetic Solid	Composition Carrier Liquid	Stabilizing Agent	Fluid Magnetization, gauss at		
				500 oe	1000 oe	10000
1015	Magnetite	Kerosene	Tenlo 70	186		380
1028	Magnetite	Mineral oil	Tenlo 70	270		560
1030	Magnetite	Tetrahydronaphtalene	Oleic acid	90	130	250
1032	Magnetite	Kerosene	Tenlo 70	90		137
G 80B	Magnetite	Water	Tamol 731	42		58

γ = permanent magnetic dipole of a particle

R = center-center separation of interacting particles

d = particle diameter

M_s = saturation magnetization

This equation suggests that the magnetic viscosity effect becomes more pronounced as the particle size increases, as was indeed found. It is also expected that as the particle concentration increases particle to particle interactions should increase. Fluid 1028 shows a greater effect than fluid 1015, however, the carrier fluid is different in the two cases even though the particles come from the same grind.

The magnetic interaction effect is more marked at low shear rates than at high shear rates. Since the system is sheared at right angles to the field, fluid motion will tend to disalign the particle moments from the field direction. At low shear rates, the particles will have a greater tendency to align than at high shear rates.

The data obtained to date are the first of their kind. The small effect of magnetic fields which lead to 50% of saturation of fluids 1015 and 1030 is encouraging. The marked effect noted with fluid G 80B was considered the expected behavior of ferrofluids in analogy with the solidification of magnetic clutch suspensions.

One of the major drawbacks of the data obtained to date is that the measurements are limited to low fields which do not completely align the particles. This is due to the limitations of air-cooled coils used to date. Water cooled coils have been procured which should permit operation with higher fields. If these coils cannot generate a field of 10,000 oe over the volume necessary to make the measurements, the National Magnet Laboratory at MIT (Cambridge) will be contacted in order to obtain permission to use the equipment that is available there.

A second drawback to the data collected is that a systematic parametric study of the major variables was not performed. In the following quarter, at least one ferrofluid will be investigated in more detail, in order to determine the effects of field strength, field orientation and fluid magnetization on the magnetic viscosity effect.

D. PREPARATION OF THERMALLY STABLE ORGANIC FERROFLUIDS BY THE "OVERSHOE" PROCESS

It was originally proposed to prepare a thermally stable organic base ferrofluid by grinding in the presence of a surfactant that would be polymerized on the surface of the particles. This would result in a polymerized overshoe that would still cover the surface even if the bond holding the particle to the surface would be broken. Since it is believed that thermal flocculation is due to destruction of the stabilizing layer by desorption, the above technique would result in more stable ferrofluids.

It was originally proposed to prepare such fluids by grinding in the presence of multi-unsaturated fatty acids such as linolenic or eleostearic acid and by polymerizing these acids by catalytic oxidative free radical reaction, the mechanism which controls the "drying" of paints.

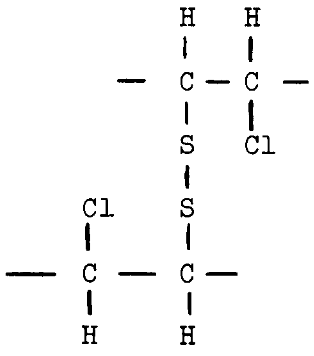
Preliminary experiments with bulk solutions of different fatty acids in kerosene indicated an extremely slow rate of reaction below 100°C even in the presence of a peroxide initiation and metal salt catalyst. The reaction also occurred with the surface film at the solution/air interface which slowly thickened with time over a period of weeks. These results indicated that the reaction was limited by the rate of diffusion of gaseous oxygen to the polymerizable molecules. Due to the limited solubility of oxygen in kerosene this is an extremely slow process.

It was decided to investigate other possible systems which, in addition to all the other requirements would not be limited by mass transfer considerations. It is well known that sulfur is used to vulcanize rubber. This involves the reaction of sulfur with an unsaturated linear polymer to form a cross-linked three dimensional network. An equally well established, but less well known, system is the reaction of sulfur chlorides (sulfur monochloride S_2Cl_2 and S_2Cl_4) with unsaturated fatty glycerides to form vulcanized white oils which rubber-like compounds which are trade-marked as "factice".(2)

Overshoe formations by the sulfur chloride route utilizes the same surfactants as were originally considered for the free radical oxidation mechanism; namely, multi-unsaturated fatty acids.

The principal reaction is the addition of sulfur to the double bond as illustrated below:

$$S_2Cl_2 \; + \; 2\,(\; - \; CH = CH \; - \;) \longrightarrow$$



This reaction is quantitative and proceeds rapidly at room temperature. Sulfur chloride is very soluble in hydrocarbon solvents such as kerosene. The reaction is highly exothermic. Care has to be taken to prevent overheating of the system which would result in decomposition of the molecules as evidenced by discoloration and HCl formation.

Ferrofluids have been successfully prepared with a variety of unsaturated fatty acids including oleic acid (singly unsaturated) linoleic acid (doubly unsaturated) and linseed oil fatty acid (principal component - linolenic acid which is triply unsaturated).

Preliminary polymerization tests have been carried out with bulk samples of the above fatty acids, and with linseed oil which is the natural triglyceride of linseed oil fatty acid. In these tests, 12.5 cc of 4 molal sulfur chloride solution (0.05 mole of S_2Cl_2) were added to 14 gr of fatty acid ($\sim$0.05 mole) in a 100 ml beaker. The system was stirred and allowed to stand. No special provisions were taken to cool the samples. Both sulfur monochloride (S_2Cl_2) and sulfur dichloride (SCl_2) solutions were used.

The results obtained are summarized in Table V. Polymerization occurs very rapidly when multi-unsaturated acids are used. The evidence for this is a great increase in the viscosity and consistency of the samples. With oleic acid there was evidence of reaction to the dimer as noted by an increase in temperature of the system; a change in color and a slight increase in viscosity. However, because there is only one reactive site, there was no chain formation as must have occurred with the multi-unsaturated species.

Further tests were performed with linseed oil fatty acid in which the amount of S_2Cl_2 added was varied between 0.5 mole/mole fatty acid and 1.5 moles/mole fatty acid. In order to prevent overheating, the test vessels were immersed in an ice bath. System temperature was maintained between 5°C and 15°C during the addition of S_2Cl_2. When less than 1 mole/mole was added (0.5 and 0.75) the linseed oil fatty acid was transformed into a homogeneous viscous material. When more than 1 mole/mole was added, two phases were formed: a very viscous polymeric material and a thin supernatant layer (kerosene). There was also some sulfur present in the supernatant layer.

These preliminary tests were very encouraging in that monomeric polyunsaturated fatty acid could be transformed rapidly into a kerosene soluble polymer by addition of a sulfur chloride solution in kerosene.

Tests were then performed with a ferrofluid. As previously reported a ferrofluid was made by grinding magnetite in kerosene in the presence of linseed oil fatty acid - (grind G 63). A sample of this ferrofluid spun at 2000 gee for 1 hour was used in these experiments. This liquid had a saturation magnetization of 75 gauss. This corresponds to a magnetite concentration of 1.35% by volume, and from the initial ratio of fatty acid to magnetite in the original mix, a fatty acid concentration of 10% by weight. Three 10 ml aliquots of ferrofluid, containing 3.6 millimoles of linseed oil fatty acid, were treated 1.8 millimoles, 1.0 millimoles and 0.03 millimoles of sulfur dichloride respectively.

Table V

Effect of Sulfur Chloride Addition On Unsaturated Fatty Acids

	Additive	
Fatty Acids	Sulfur Monochloride	Sulfur Dichloride
Oleic Acid	Slight increase in viscosity	Increase in viscosity
Linoleic acid	Viscous tar	Viscous tar
Linseed oil fatty acid (linolenic acid)	Viscous tar	Viscous tar
Unbodied Linseed Oil (Linolenate triglyceride)	Rigid gel	Popcorn polymer

As a result of this treatment, the first two samples were tranformed into a gel with some synerisis occurring. The last sample had become slightly more viscous. These samples were examined the following day. In the first two samples, two layers had formed - a thick gel and a separate liquid phase. The third sample had also formed two layers: a viscous tar on the bottom and a thin liquid on top. These layers mixed easily upon stirring. The viscosity of this mixture was measured at 33°C over a shear rate range of 23 sec^{-1} to 230 sec^{-1}. The untreated fluid had a viscosity of 2.1 cp at this temperature over this shear rate range. These results indicate that polymerization had occurred as a result of the addition of S_2Cl_2 to the ferrofluid. However, the polymerization was not limited to the particle coating where it was desired but occurred in the bulk liquid phase as well which is undesirable. The separation of a gel in the first samples could have occurred as a result of particle coupling by polymerization in the bulk phase.

The bulk phase polymerization was considered due to the presence of excess linseed oil fatty acid molecules in the bulk phase. In order for these experiments to be successful this excess monomer has to be removed. This means that the particles coated with the surfactant have to be physically separated from the carrier liquid.

In order to carry out this separation, 200 cc of isopropyl alcohol was added to 40 cc of ferrofluid. This resulted in flocculation of the suspension. The liquor was centrifuged to achieve spearation of the solid and liquid phases. The supernatant liquid was discarded. 60 ml of fresh kerosene was added to the solids and shaken for 2 hours. The solids redispersed to form a ferrofluid with a saturation magnetization of 42 gauss. From the relative volumes of the stabilizing sheath and the magneticcore that constitute the particle, assuming a sheath thickness of 35 Å and a core size range of from 50 Å to 100 Å, a 10 gram sample of this redisperded ferrofluid contains from 0.7 to 3.5 millimoles of fatty acid. Varying quantitites, ranging from 0.5 ml to 4.0 mil, of 0.5 Normal S_2Cl_2 solution in kerosene were added to 10 gr aliquots of ferrofluid.

In all cases, the addition of sulfur dichloride solution resulted in flocculation of the ferrofluid. There was complete separation of the solids from the supernatant liquid phase when centrifuged at 2000 gee for 10 minutes. The supernatant was clear.

The flocculation could be due to either 1) interparticle chaining as a result of the polymerization of unsaturated molecules on adjacent particles, either directly or through the intermediary of fatty acid molecules dissolved in the liquid phase; 2) modification of the absorbed sheath around the particles so that the structure which prevents flocculation is destroyed.

The first argument is discarded for the following reasons:

1. The particle concentration is very low. The volumetric concentration of magnetite is only 0.75%. The volume concentration of sheathed particles

can be at most 4%. The probability of interparticle contact is small. As a result of the flocculation redispersion step, the only free fatty acid molecules dissolved in the bulk phase are those which desorbed from the particles to maintain equilibrium. If it is assumed that the absorption coefficient is very close to unity, there is only a negligible fatty acid concentration existing in the bulk phase.

A more likely explanation is that the adsorbed sheath is modified. It had been previously reported (Quarterly Report No. 1) that Chinawood fatty acid, which is essentially eleostearic acid, which contains three conjugated double bonds, was not a successful stabilizing agent, whereas less unsaturated 18 carbon fatty acids, such as oleic acid and linoleic acid, did result in ferrofluid formation.

The principal component of linseed oil fatty acid, linoleic acid, contains three unconjugated double bonds. It was argued that a stable solvent - fatty acid tail sheath is not formed when the fatty acid molecule is rigid. The order of molecular rigidity is eleostearic acid > linolenic acid > linoleic acid > oleic acid. Therefore, a stable ferrofluid was not formed in the presence of eleostearic acid.

Structural rigidity of the stabilizing sheath can also be used to account for the flocculation which occurs when sulfur dichloride is added to a linolenic acid stabilized ferrofluid. Adjacent molecules are coupled to form a more rigid structure which excludes solvent molecules. The adsorbed monolayer essentially now acts as an extension of the solid substrate and the protection against interperticulate forces that previously existed, disappears.

This argument indicates that a stabilized monolayer cannot be made because the polymerization steps destroy the solvation capacity of the monolayer.

These results and the argument used to account for these results are of basic importance to the concepts that exist about the stability of ferrofluids. What are the permissible structural characteristics of the adsorbed layer " vis - a - vis" the structural characteristics of the solvent? Is there one ideal surfactant for a given solvent system (a one-to-one match) or is there a range of permissible agents? The second suggested by the fact that oleic acid, linoleic acid and linolenic acid among other surfactants all resulted in ferrofluid formation.

It is possible that addition of sulfur dichloride in judicious quantities to oleic acid or linoleic acid ferrofluids will polymerize the molecules and yet not destroy the solvation of the adsorbed layer (and therefore result in flocculation).

It is planned to carry out the following experiments in the near future: 1) addition of sulfur chloride to an oleic acid stabilized ferrofluid to determine whether flocculation results; 2) if the oleic experiment does not result in flocculation, addition of sulfur chloride to a linoleic acid stabilized ferrofluid, in an other attempt to form an overshoe. This ferrofluid is now being prepared (grind G 120).

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