RESEARCH IN THE SYNTHESIS AND CHARACTERIZATION

OF MAGNETIC FLUIDS

(PHASE II)

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This is a first 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 being carried out in the Ferrohydrodynamics Section which is under the leadership of Dr. R. E. Rosensweig. The principal scientific investigator is Dr. R. Kaiser. Further section personnel who also participated in the effort in this quarter were Mr. G. Miskolczy and Mr. N. Sheppard.

ABSTRACT

Ferrofluids are prepared by dispersing a magnetic powder in a liquid in the presence of a stabilizing agent. A grinding program was initiated that incorporates the following goals:

1) Study of formation of ferrofluids in organic non-polar media.

2) Preparation of ferrofluids in other media such as water.

3) Preparation of ferrofluids of higher magnetic saturation and susceptibility.

4) Preparation of thermally stable ferrofluids.

5) Process improvements studies.

A water base fluid has been prepared for the first time.

Geometric requirements for a colloidal dispersion with a high volume concentration of magnetic solids are discussed. These indicate that magnetite fluids of higher magnetic strength than have been attained to date (1000 gauss) are feasible.

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A. INTRODUCTION

Avco Corp. has been actively studying ferromagnetic liquids since 1963. These ferrofluids are dispersions of magnetic solid in a liquid that are stabilized by the addition of a surface active agent. An extensive amount of exploratory research under the sponsorship of NASA - OART led to fluids of improved magnetic properties, the discovery of a number of unusual phenomena such as the formation of magnetic liquid spikes and the buoyant levitation effect, and initial characterization of the physical properties of these ferrofluids in terms of the basic physical parameters of the system. These results have been described in detail in a recently published report by Rosensweig and Kaiser (Reference 1).

The applicability of ferrofluid prepared to date is limited by their magnetic characteristics, their temperature stability and the physical properties of the carrier liquids (specifically kerosene and similar hydrocarbons and chlorocarbons).

The goals of the present program phase are to prepare ferrofluids of improved magnetic properties (higher magnetization and susceptibility), greater temperature stability, and different base solvents and to obtain further a fundamental knowledge of the behavior of these unusual liquids.

This report describes the overall program, key experimental and theoretical results obtained, current problems and proposed corrective action.

B. General Preparative Procedure

The ferrofluids are prepared by prolonged grinding of magnetic powder in a ball mill in the presence of a solvent and a stabilizing agent. A grinding run is considered successful when a fluid dispersion of magnetic particles is obtained that is stable under the influence of gravity and magnetic field gradients. Unsuccessful grinding runs are characterized by either separation of the solid and liquid phases in either a gravitational or magnetic field or the formation of an intractable gel that cannot be broken either by addition of further solvent or surfactant.

The liquid product of a successful run is then normally centrifuged at 17000g for 10 minutes to remove oversized particles nominally larger than $350 \cdot \overset{\circ}{A}$. This product is a basic raw material that can then be modified in numerous ways: vacuum evaporation to increase magnetic moment and viscosity, solvent exchange to alter certain properties of the fluid, centrifugation to modify particle size distribution, etc.

1. Characterization of Ferrofluids

The principal physical properties of the ferrofluids which are of interest are particle size distribution of the magnetic colloid, the magnetic characteristics of the suspension, the flow characteristics of the suspension and the density of the suspension. The particle size distribution of the particles in suspension is obtained by examination of electron photomicrographs. The magnetic properties of a ferrofluid are obtained by a standard search coil technique under applied magnetic fields in the range from 116 oersted to 10,000 oersted.

The flow properties are measured in a Wells Brookfield cone/plate microviscometer which was acquired for the program. In this device, fluid is placed between a plate and a cone, the cone being rotated at constant speed. Viscosity is measured in terms of the resistance offered by the test fluid to flow under constant rotation conditions, the viscous fluid resistance being opposed by a center balancing torque that is provided by a helical spring connected to the rotor shaft. The viscosity is directly proportional to this applied torque. As the angle between the cone and plate is small, the shear rate in the liquid is uniform throughout bulk. As one is dealing with a thin film, the fluid is maintained between the cone and plate by capillary action. Furthermore, since the sample is a thin film, precise temperature control is easily manintained.

This cone and plate viscometer is well suited to the needs of the present research effort since:
   a) a very small sample (1.0cc) is required for the measurement.

   b) The standard operating range of the instrument is 0-2000cp, the viscosity range of most useful ferrofluids.

   c) It is possible to measure the viscosity of a fluid at different discreet shear rates which range from 1.15 sec^{-1} to 230 sec^{-1}.

d) It is possible to determine whether the viscosity of a fluid is time dependent by studying the rate of torque relaxation. In this test procedure, the helical spring is rotated to a maximum torque reading and locked in position. The fluid is then placed in the instrument. The spring is then released and the torque is then measured as a function of time. (Reference 2).

The density of the ferrofluid is obtained by measuring the weight of a sample of known volume in a tared pycnometer.

C. Grinding Runs (Table I)

The series of grinding runs initiated in the first phase of the program was continued. In Phase I, emphasis was placed on screening various surfactants that would result in magnetite base ferrofluids in hydrocarbon carriers. This aspect of the work is presently being continued. A number of other goals have been incorporated into the grinding program. These include:

1) Preparation of ferrofluids in carrier liquids other than hydrocarbons, in particular, water and other polar media.

2) Preparation of magnetite base ferrofluids of higher ultimate saturation magnetization then has been possible in the past (i.e. 1000 gauss).

3) Preparation of ferrofluids with magnetic solids that have a higher saturation magnetization than magnetite.

4) Process improvement studies with previously successful surfactant/solvent systems.

1. Preparation of Water Base Ferrofluids

All ferrofluids prepared in the past have been oil based fluids. For many applications there is a need for water soluble or water-compatible fluids.

As in non-aqueous media, there are forces of attraction between solid particles suspended in aqueous media which lead to flocculation. It is possible to defloculate such suspensions by adding surface active materials which adsorb strongly at the solid-aqueous interface and which overcome the strong interparticle attraction. In water the principal repulsive forces are electrostatic in origin, rather than entropic repulsion, since water is an ionizable liquid with a high dielectric constant. Two principal factors which determine the effectiveness of a solid dispersant in water are the ability of the dispersant to (1) adsorb on the surface of the solid particle and (2) impart a high charge density.

Typical products that have been successfully used to disperse solid pigment particles ($D \cong 0.1\mu$ to 10μ) in water include sodium polyphosphates, sodium salts of lignin sulfonic acids, sodium salts of arylalkyl sulfonates and sodium salts of carboxylated electrolytes. In addition to the above which are low molecular weight polyelectrolytes, fatty acid soaps and some proteins also have dispersing properties.

TABLE I

TABULATION OF GRINDING RUNS

Key to Comments:

I.   Successful ferrofluid formed with initial mixture of ingredients

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
4.7 pint	625	50	20
1.6 gal/2.0 gal	1250	100	40
3.0 gal	3750	300	120

TABLE I (CONT'D)

Charge	Carrier Fluid	Dispersant	Dispersant Formula	Magnetic Powder	Time (Hrs.)	Comments
G-61 1.6 gal	Kerosene	Chinawood Fatty Acids (Eleostearic Acid)	$CH_3(CH_2)_3(CH=CH)_3(CH_2)_7COOH$	Magnetite $FeO.Fe_2O_3$	1620	V
G-62 1.6 gal	Kerosene	Dodecyl Amine (1.0 gm/gram solids)	$CH_3(CH_2)_{11}NH_2$	Magnetite $FeO.Fe_2O_3$	2021	I C
G-63 1.6 gal	Kerosene	Linseed Oil Fatty Acids (Linolenic Acid)	$CH_3(CH_2CH=CH)_3(CH_2)_7COOH$	Magnetite $FeO.Fe_2O_3$	2327	IV A
G-64 1.6 gal	Heptane	Oleic Acid	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	Magnetite $FeO.Fe_2O_3$	2189	IV B
G-65 2.0 gal	Kerosene	Linseed Oil (Glyceryl tri-linolenate)	$CH_3(CH_2CH=CH)_3(CH_2)_7COOCH_2$ $CH_3(CH_2CH=CH)_3(CH_2)_7COOCH$ $CH_3(CH_2CH=CH)_3(CH_2)_7COOCH_2$	Magnetite $FeO.Fe_2O_3$	1975	VI
G-66 1.6 gal	Kerosene	Oleic Acid (0.1 cc/gram solids)	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	Magnetite $FeO.Fe_2O_3$	1289	Gasket Failure
G-67 4.7 pint	Kerosene	Hexadecyl Amine	$CH_3(CH_2)_{15}NH_2$	Magnetite $FeO.Fe_2O_3$	559	I C
G-68 4.7 pint	Kerosene	Myristic Acid	$CH_3(CH_2)_{12}COOH$	Magnetite $FeO.Fe_2O_3$	1037	VI

TABLE I (CONT'D)

Charge	Carrier Fluid	Dispersant	Dispersant Formula	Magnetic Powder	Time (Hrs.)	Comments
G-69 4.7 pint	Tetrahydro-naphthalene	Cinnamic Acid	$\bigcirc$—CH=CHCOOH	Magnetite FeO.Fe$_2$O$_3$	241	VI
G-70 1.6 gal	Water	Tamol 731	Sodium Salt of a Poly-carboxylic Acid	Magnetite FeO.Fe$_2$O$_3$	400	VII
G-71 3 gal	Kerosene	Oleic Acid	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	Magnetite FeO.Fe$_2$O$_3$	39	Gasket Failure
G-72 3 gal	Kerosene	Oleic Acid	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	Magnetite FeO.Fe$_2$O$_3$	3038	I B
G-73 4.7 pint	Kerosene	Duomeen L 11	$CH_3(CH_2)_9CHCH_3$ $NH(CH_2)_3NH_2$	Magnetite FeO.Fe$_2$O$_3$	1400	I C
G-74 1.6 gal	Water	Tamol 731	Sodium Salt of a Poly-carboxylic Acid	Magnetite FeO.Fe$_2$O$_3$	426	VII
G-75 1.6 gal	Kerosene	Oleic Acid (0.2 cc/gram solids)	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	Magnetite FeO.Fe$_2$O$_3$	2219	III B
G-76 1.6 gal	Water	Tamol 850	Sodium Salt of a Poly-carboxylic Acid	Magnetite FeO.Fe$_2$O$_3$	1520	VII

TABLE I (CONT'D)

Charge	Carrier Fluid	Dispersant	Dispersant Formula	Magnetic Powder	Time (Hrs.)	Comments
G-77 1.6 gal	Kerosene	Tenlo 70	Oil Soluble nonionic surfactant. Condensation product of an amino ester of a fatty acid	Magnetite $FeO.Fe_2O_3$	1124	I A
G-78 1.6 gal	Kerosene	Tenlo 70 (0.3 cc/gram solids)	see G-77 above	Magnetite $FeO.Fe_2O_3$	1706	III A
G-79 1.6 gal	Kerosene	Tenlo 70 (0.2 cc/gram solids)	see G-77 above	Magnetite $FeO.Fe_2O_3$	1890	III A
G-80 1.6 gal	Water	Tamol 731 (1.0 cc/gram solids)	Sodium Salt of a Poly-carboxylic acid	Magnetite $FeO.Fe_2O_3$	651	I A
G-81 4.7 pint	Kerosene (dry)	Santopoid 23 RI	Extreme Pressure Gear Oil Additive	Cobalt-Iron (35% Cobalt)	330	VI
G-82 2.0 gal	Kerosene	Tenlo 70	see G-77 above	Magnetite $FeO.Fe_2O_3$	1467	I A
G-83 4.7 pint	Kerosene (dry)	Oleic Acid	$CH_3-(CH_2)_7CH=CH(CH_2)_7COOH$	Cobalt-Iron (35% Cobalt)	1315	In progress
G-84 4.7 pint	Kerosene (dry)	Oleic Acid	$CH_3-(CH_2)_7CH=CH(CH_2)_7COOH$	Cobalt-Iron (35% Cobalt)	1315	In progress Tungsten Carbide Balls

TABLE I (CONT'D)

Charge	Carrier Fluid	Dispersant	Dispersant Formula	Magnetic Powder	Time (Hrs.)	Comments
G-85 1.6 gal	Kerosene	Tenlo 70	See G-77 above	Magnetite FeO.Fe$_3$O$_4$	1143	In Progress Magnetite Concentra- tion: 4.7%
G-86 1.6 gal	Water	Blancol N	Polymeric Sodium Naphtha- lene Sulfonate-Formalde- hyde Condensate	Magnetite FeO.Fe$_2$O$_3$	484	VI
G-87 1.6 gal	Water	Tamol 850	Sodium Salt of a Poly- Carboxylic Acid	Magnetite FeO.Fe$_2$O$_3$	571	In Progress
G-88 1.6 gal	Water	Lomar D	Sodium Salt of Polymerized Naphthalene Sulfonate	Magnetite FeO.Fe$_2$O$_3$	526	In Progress
G-89 1.6 gal	Kerosene	ENJAY 3029	High Temperature Polymeric Oil Soluble Dispersant	Magnetite FeO.Fe$_2$O$_3$	479	In Progress
G-90 1.6 gal	Kerosene	ENJAY 3355	High Temperature Polymeric Oil Soluble Dispersant	Magnetite FeO.Fe$_2$O$_3$	480	In Progress
G-91 2.0 gal	Kerosene	Tenlo 70 (0.3 cc/gram solids)	See G-77 above	Magnetite FeO.Fe$_2$O$_3$	320	In Progress

Polyelectrolytes appear to be more effective dispersing and suspending agents for a variety of particulate materials. The effectiveness of a polyelectrolyte dispersant lies in its being able to impart a high charge density to a pigment particle. This depends on the number of ionizable groups in the dispersant molecule. Capacity to impart charge density increases as the number of charged sites introduced into one molecule increases. However, the size of the dispersant molecule is limited since, if the molecule becomes too large, it could adsorb into two or more particles and result in flocculation.

It has been found that a great deal of specificity exists in the adsorption of dispersants on the surfaces of solid particles. For example, naphthalene sodium sulfonate does not adsorb at all on anastase titanium dioxide and is poor dispersing agent whereas a desulfonated lignosulfonate is adsorbed and is an excellent dispersant (Reference 3). Similarily, good performance by a particular dispersant on one pigment does not assume similar effectiveness on another pigment.

Further difficulties for the particular problem at hand is the fact that most commercial dispersants might not have any specific action as a grinding aid and the fact that the particles that one desires in a ferrofluid are of the order of 100 $\overset{o}{A}$ in diameter, which places limitations on the molecular weight (i.e. chain length) of the polyelectrolyte that could be used as a dispersant.

A number of manufacturers were contacted and samples of commercial dispersing agents were obtained. These dispersants included:

a)   Tamol 731 (Rohm and Hass Co.). This is a sodium salt of carboxylated polyelectrolyte that is used to disperse a variety or organic and inorganic pigments.

b)   Tamol 850 (Rohm and Hass). This is also sodium salt of a carboxylated polyelectrolyte, of longer chain length then Tamol 731, that is a dispersant for clays and inorganic pigments.

c)   Blancol N (General Aniline and Film Co.). This is an anionic polymeric sodium naphthalene sulfonate – formaldehyde condensate widely used in the paper industry as a dispersing agent for paper filler.

d)   Lomar D (Nopco Chemical Co.). This is the sodium salt of a highly polymerized naphthalene sufonate. The manufacturer recommends it in any application involving the dispersing of solid particles in aqueous media and reducing the viscosity of solids dispersed in water.

A first series of runs were carried out using these various polyelectrolytes as the stabilizing agent. The results were very encouraging.

Tamol 731 proved to be an effective dispersing agent if present in sufficient enough quantity, as evidenced by the results presented in Figure 1. In all three runs where this material was used as the dispersant there was initial magnetic colloid formation. In the first two runs (G70–G74) where 0.50 cc of Tamol 731 solution was added per gram of magnetite there was an increase in colloid concentration with time until grinding time approached 400 hours. In both cases,
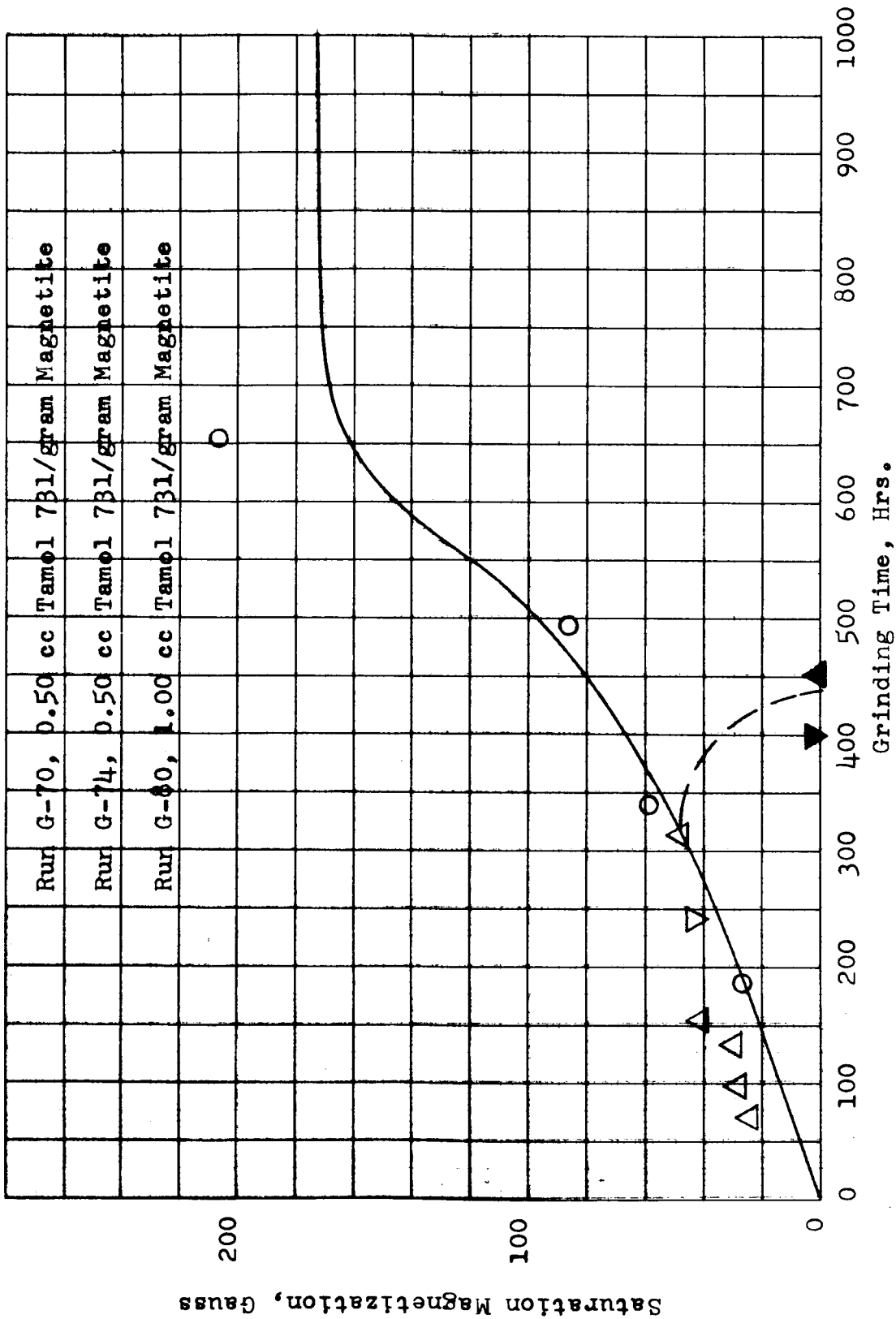
Figure 1 Effect of Stabilizer Concentration on the Formation of a Water Base Ferro-
fluid.

when the grinding mills were opened, the previously stable colloidal suspension had flocculated and the magnetic solid separated form solution. It is estimated that the magnetic moment of the colloid just prior to flocculation was about 50 gauss. In a third run (G80) the stabilizer concentration was increased to 1.00 cc per gram of magnetite. In this case, it was possible to incorporate more magnetite without flocculation. After 500 hours of grinding, the magnetization of the fluid was about 84 gauss and no evidence of flocculation. After 650 hours of grinding it was observed that there was an increase in fluid viscosity. It was difficult to spin the sample down at 2000g in a laboratory centrifuge so that the measurement of magnetization and density at this time are subject to error because of inhomogeneities. The measured magnetization M=215 gauss is in fact 30% higher than would be predicted on the basis on the volumes of the initial ingredients (M_{max} = 170 gauss).

It was decided to stop the grind at this point in order to study the properties of the resulting ferrofluid, even though the thickening of the batch was evidence of incipient flocculation.

It should be noted that the grinding rate obtained with these runs was higher than the rates observed with any kerosene base ferrofluids. It also appears to be independent of the stabilizer concentration.

Two runs were performed with Tamol 850. In a first run (G76) as shown in Figure 2, which had a stabilizing agent concentration of 0.50 cc/gram, initial colloid formation was observed followed by flocculation at 600 hrs of grind. Continued grinding accompanied by further addition of Tamol 850 did not repeptize the colloid. A second run was started with a concentration of 1.00 cc/gram magnetite (G87). The run is presently in progress: up to 400 hrs., an increase in colloid formation with time was observed. Based on the limited information available to date, with Tamol 850, as with Tamol 731, it appears that the rate of grind is independent of concentration of the stabilizing agent. The rate of grind with Tamol 850 appears to be half the rate of grind with Tamol 731.

The sodium naphthalene sulfonates (Blancol N and Lomar D) did not result in a satisfactory product to date. In a run with Blancol N (G86) there was complete separation of magnetic particles after 480 hrs. With Lomar D, in a run still in progress (G88), the fluid is only slightly magnetic after 366 hours.

2. Preparation of Ferrofluids with Materials of Higher Saturation Magnetization

In phase I of the program three separate attempts to prepare ferrofluids by iron powder in kerosene in the presence of different surfactants resulted only in very weak colloid formation. The powder used in these experiments was iron carbonyl powder type L by the General Aniline and Film Co. This is a very pure grade of iron which is physically soft and easily compressed. The initial particle size of the material was about 6-9 microns.
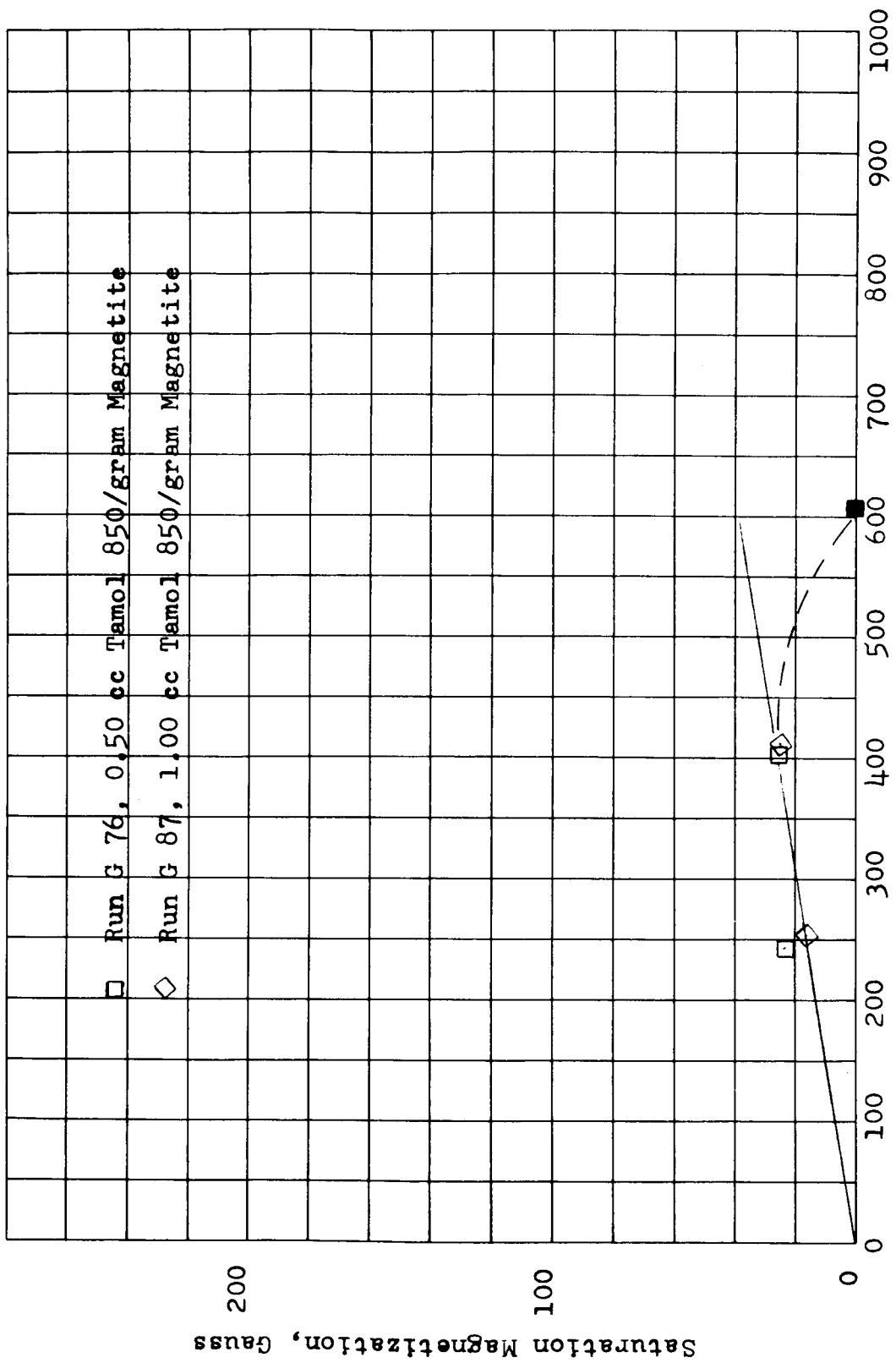
Fig. 2 Effect of Stabilizer Concentration on the Formation of a Water Base Ferrofluid

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The difficulties encountered in the previous grinding runs were believed due to:
1) The fact that the powder was easily deformable and would therefore not break into smaller fragments during the grinding process.

2) The presence of impurities in the carrier that could oxidize the iron powder.

3) Reaction between the surfactant and the powder leading to decomposition of either component.

In order to try to overcome these difficulties the following steps were taken:
1) Use powders of magnetic alloys that are hard and brittle so that abrasion rather than deformation would occur in the grinding operation. Alloys of particular interest were:
   a) Iron-cobalt alloy powders with a 35% cobalt content corresponding to the alloy Fe_2Co. This alloy has a saturation magnetization of 24,300 gauss which is 13% higher than pure iron. This material is also hard and brittle.

   b) Iron-Silicon alloys with approximately 14% silicon (corresponding to Fe_3Si) exhibit high permeability and are very brittle, supposedly easily reduced to a powder state.

Powders of the above composition were purchased. Since these powders cannot be made by chemical decomposition, the finest particle size material available is one order of magnitude higher than the iron carbonyl powder previously used. These powders were sold as nominally - 200 mesh material (200 mesh = 74 microns). The grinding time is expected to be much longer with this material.
2) To eliminate impurities such as water and oxygen, all operations are carried out with dry reagents and under conditions of minimum oxygen contamination.

3) The ideal surfactant for such systems would be one that would adsorb on the metal surface but would not undergo decomposition after adsorption and would not greatly alter the bulk of the metal phase. It was thought that compounds that might prove to be satisfactory in such experiments would be chemicals that have found use as extreme pressure lubricants or cutting oil additives, usually materials that contain phosphorus, sulfur or halogen in the molecule. These compounds are believed to strongly adsorb on bearing metal surfaces but not to react with the metal to form gross phases of metallic compounds. An example of materials of this type would be zinc dialkyl dithiophosphate (Monsanto Santotube 393 oil additive).

In addition to the above, a grinding mill was also equiped with tungsten carbide grinding balls. These balls are much harder with more abrasion resistance and denser (ρ =14.9 gr/cm^3) than the hardened iron balls normally used in the grinding operation. Assuming the grinding operation to be due to an impact process, the rate of grind should increase with the difference in density between the balls and the liquid medium. The rate of grind should also increase with decreasing deformability

of the grinding medium.

Three grinding runs were started with the 35% cobalt-iron alloy powder (G81, G83, G84). Two runs were made with oleic acid as standard additive, G83 with standard balls and G84 with tungsten carbide balls. In both runs the rate of grind is very slow, after 1155 hrs. of grinding a dark colored supernatant was formed that was too weak magnetically to measure. Grinding will be allowed to continue for another 500 hrs. If no magnetic response is detected by then, the runs will be stopped.

Prior to these two calibrating runs, a short run was made with Santopoid 23-RI gear oil additive. After 330 hrs. a dark liquid was obtained with no magnetic response and the run was discontinued at this time.

It is proposed to continue further metal grinding runs with the 14% silicon-iron powders in the hope that it will be easier to grind then the cobalt/iron mixture. Attempts will be made to grind with other grades of reduced carbonyl iron powders that are physically harder than the powder used in Phase I of this program. Samples of carbonyl iron powders SF and W have been ordered from General Aniline and Film Co. These powders differ from the original low carbon powder used (Grade L) in that grade SF contains 0.8% carbon while grade W contains 0.8% carbon and 6.0% nitrogen, the nitride and carbide phases increasing the hardness and presumably the brittleness of the material. These powders also have a smaller particle size then Grade L: 3 micron average diameter as compared to 8 micron average diameter.

3. Further Search for New Surfactants for Magnetite/Kerosene Systems

The search for new dispersing agents suitable to the preparation of hydrocarbon base magnetite ferrofluids was continued.

    a) Amines: In phase I it was observed that dodecyl amine and octadecyl amine produced stable colloidal dispersions. With both these chemicals the rate of grind was much slower than oleic acid. A waxy film was observed to form at the surface of the ferrofluids so obtained that increased in thickness with time. It was believed due to the limited solubility of the amines in the hydrocarbons used. It was further found that octyl amine did not result in the formation of a stable colloid.

To complete the work on aliphatic amine surfactants in hydrocarbon solvents, three more runs were made:

    1) Dodecyl amine:(1.0cc/gram magnetite) (G62). The results were similar to those previously obtained with this additive at a level of 0.5cc/ gram magnetite. After 2000 hrs. of grind the magnetization of the fluid was only 23 gauss.

    2) Hexadecyl amine:(G67). The results obtained with this amine are analogous to these obtained with dodecyl and octadecyl amines. After 559 hrs. of grind, the saturation magnetization had only reached 6.6 gauss, so the run was discontinued.

compositions of these oils are highly proprietory. The Standard Oil Co. of N. J. however, did provide samples of different dispersants which they use as dispersants. These are polybutenes which contain from 500 to 1000 carbon atoms and that have been reacted with other chemicals (unspecified) to make them surface active. It is claimed that these dispersants will stabilize colloidal dispersions in lubricating oil at temperatures as high as $600^\circ F$.

Three of the additives received, ENJAY 3029, ENJAY 3355 and ENJAY 3854, were found to be effective dispersants in sedimentation studies. Two runs have been started (G89, G90) with the first two products listed. Both runs are in progress and formation of ferrofluid has been noted.

4. Process Improvement Studies

A number of runs were carried out with surfactant/solvent mixtures that had previously yielded ferrofluids in order to study process parameters in order to:
   a) obtain a better understanding of the mechanism of the formation of ferrofluids

   b) improve operating efficiency and

   c) assure sufficient quantities of ferrofluids for evaluation and characterization.

These runs were all carried out with magnetite IRN 100 as the magnetic pigment and kerosene as the carrier. The surfactants were either oleic acid or Tenlo 70.

a) Oleic Acid Runs:

1. Step wise addition of oleic acid:

Oleic acid was the standard surfactant used in the previous studies. In two runs (G66 and G75) it was decided to add oleic acid in incremental amounts during the run on a demand basis. In both cases, there was initial/colloid formation followed by the formation of a gel and magnetic colloid separation, which however, was remedied by the addition of further oleic acid. Upon addition of further surfactant, grinding resumed as well.

2. Production Runs:

A 3.3 gal mill was obtained in order to make ferrofluid in larger batches (G71 and G72). It has been observed that the rate of colloid formation in the larger mill is much slower than in the standard 1.6 gal mill with a standard formulation.

b) Tenlo 70 Runs:

Tenlo 70 is a proprietory product of the Nopco Chemical Co. that is widely used as a dispersant for magnetic iron oxides in the manufacture of recording tapes. In

phase I of the program, it was found that this surfactant formed a stable ferro-fluid and that the rate of colloid formation in kerosene was faster in the presence of Tenlo 70 then with any other surfactant (Run G44).

The effect of Tenlo 70 concentration was studied in runs G77, G78 and G79. The initial surfactant concentrations were respectively 0.50cc gram/magnetite.

The magnetizations of these suspensions as a function of grinding time are presented in Figure 3. The principal findings were:

1) The initial rate of colloid formation was the same for all three runs.

2) After about 200 hours of grinding, the rate of colloid formation became dependent on the concentration of Tenlo 70: increasing with increasing Tenlo 70 concentration.

3) In run G79, the rate of grind leveled off at 400 hrs. and a gel was formed at about 500 hrs. The addition of 0.20cc Tenlo 70/gram magnetite at this point, broke the gel and grinding resumed. From about 600 hrs. on, G79 behaved very similarily to G78 which had an initial Tenlo 70 concentration of 0.60cc/gram.

4) The rate of colloid formation increased in run G78 until about 800 hrs. of grinding at a magnetization of about 140 gauss for the liquid. At this point, the rate of grind became insignificant and the liquid thickened markedly. Upon the addition of 0.20 cc Tenlo 70 per gram magnetite to the mixture at about 1100 hrs. resulted in resumption of grinding as measured by increasing magnetization and density of the colloid. The run was stopped when the magnetization leveled out at about 190 gauss.

At the run for both (G79) and (G78) an additional 0.20cc Tenlo 70/gram magnetite was added to the fluid so as to raise the surfactant concentration to a uniform value of 0.50 cc/gram magnetite.

5) When 0.50 cc Tenlo 70/gram magnetite was initially added as was done in run G77, there was a continuous increase in magnetization and density of the colloidal with time until at about 1000 hours of grinding when the magnetization of the colloid was above 200 gauss. There was no gel formation very similar results were previously obtained with G44 which was run under similar conditions.

6) In all three runs the magnetization levels at the end reach a level of about 200 gauss. Based on the initial magnetite concentration at the start of the run (2.88% by volume) the magnetization of the colloid in the mill should reach a level of 164 gauss by the end of the run, once all the magnetite has reached colloidal dimensions. The higher magnetization can best be explained in terms of ball attrition, not only does the magnetite become abraded but so do the balls. A second explanation could be evaporation of the kerosene during the operation which appears
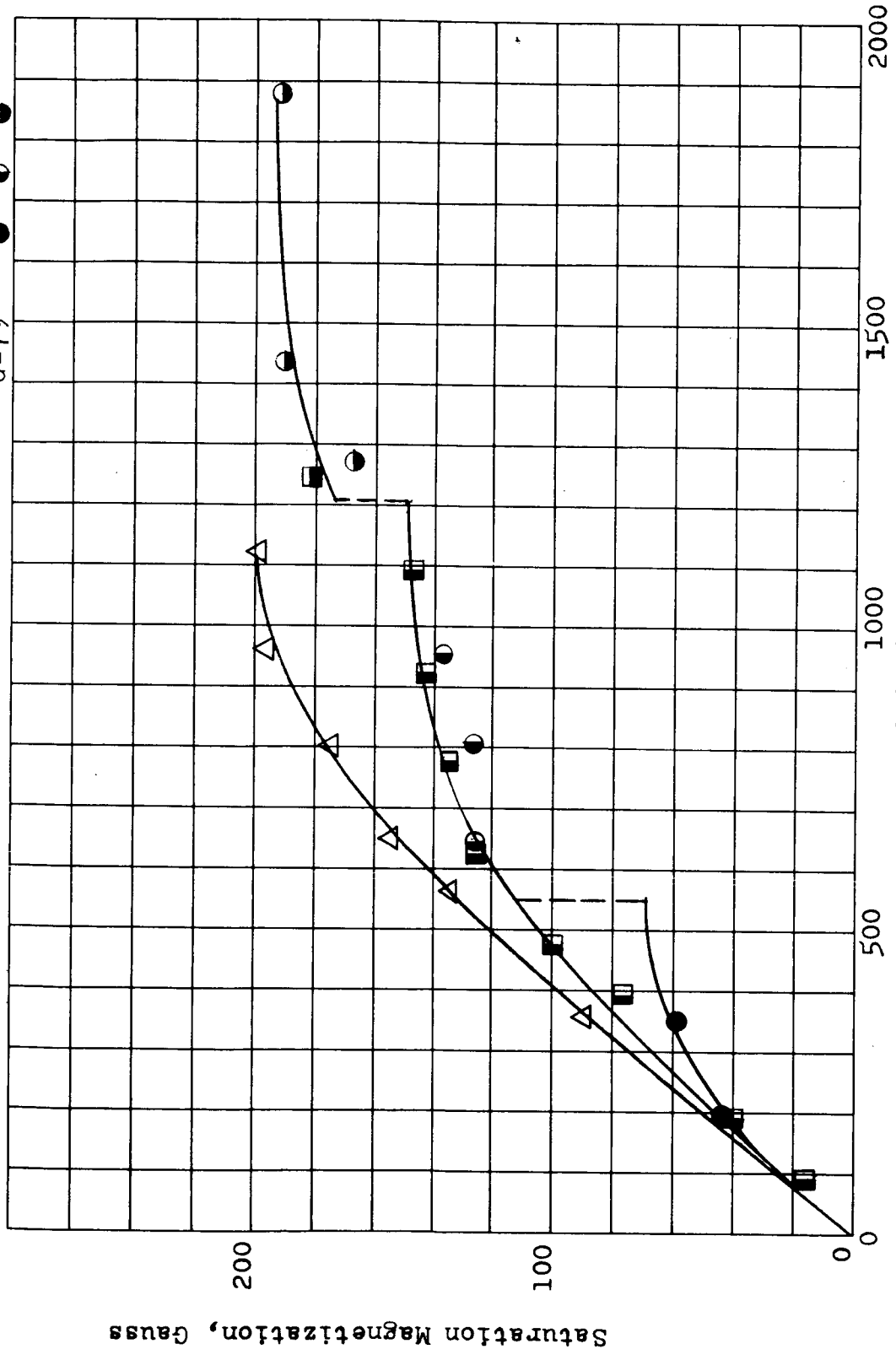
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Figure 3: Effect of Tenlo 70 Concentration on the Formation of a Magnetic Colloid

unlikely since the ball mill is a sealed system.

A run was also made with a higher magnetite concentration (4.3% by volume) at a magnetite to surfactant ratio of 0.5cc/gram, this run is still in progress (G85). It was expected that the rate of colloid formation per unit time would increase because of the higher solids concentration and higher surfactant concentration. Surprisingly the rate of colloid formation was lower as shown in Figure 4. Possible explanation might be an increase in viscosity of the liquid mixture in the mill at the higher Tenlo 70 concentration (based on total liquid volume) which would inhibit the grinding action.

Run G82 was a production run in a larger mill (2.0 gal) at a Tenlo 70 concentration of 0.50cc/gram. This mill tumbled more slowly (49 rpm) than the standard 1.6 gal mills and correspondingly the rate of colloid formula was lower, as was already discussed with oleic acid mixture G72.

D. Properties of Water Base Fluid from Grind G80

Examination of the properties of water base ferrofluid G80 is in progress. After grinding, the fluid was centrifuged at 17000g for 10 min. A large fraction of the solids in suspension were removed. These bottoms were redispersed in water and centriguged at 2000g for 10 min. The two resulting fluids were called G80T (for tops) and G80B (for bottoms).

G80T was stable for about six weeks and then turned into a gel. Further addition of surfactant redispersed the particles. The stability of this is presently being investigated. G80B is stable to date (eight weeks from preparation). Both fluids can be evaporated to dryness to form a shiny black material similar to anthracite coal in appearance. This solid can be redispersed in water to reform a ferrofluid. These fluids are miscible and compatible with ethylene glycol and glycerol. The water can be evaporated so that now one has ethylene glycol and glycerol base fluids as well. The low volatility and higher viscosity of these liquids make them more suitable bases than water for a number of practical applications since water would evaporate upon prolonged exposure to the atmosphere. All the above fluids are also immiscible in kerosene and similar nonpolar media. Addition of polar organic solvents such as acetone or ethyl alcohol results in flocculation. The flocculated material did not redisperse upon addition of fresh distilled water.

The magnetization curves of G80T and G80B fluid were obtained and are presented in Figures 5 and 6. The initial magnetization defined as the ratio of magnetization at 116 oersted to saturation magnetization, is higher for G80B than for any other fluid prepared to date. For this fluid, M_{116} = 31 gauss, M_s = 59 gauss, so that M_{116}/M_s = 0.525. The initial permeability of this fluid is 1.27. It is noted with great interest that a ten fold concentration of this fluid by normal techniques should yield a fluid with an initial permeability of 3.7 which is higher than has been obtained to date.
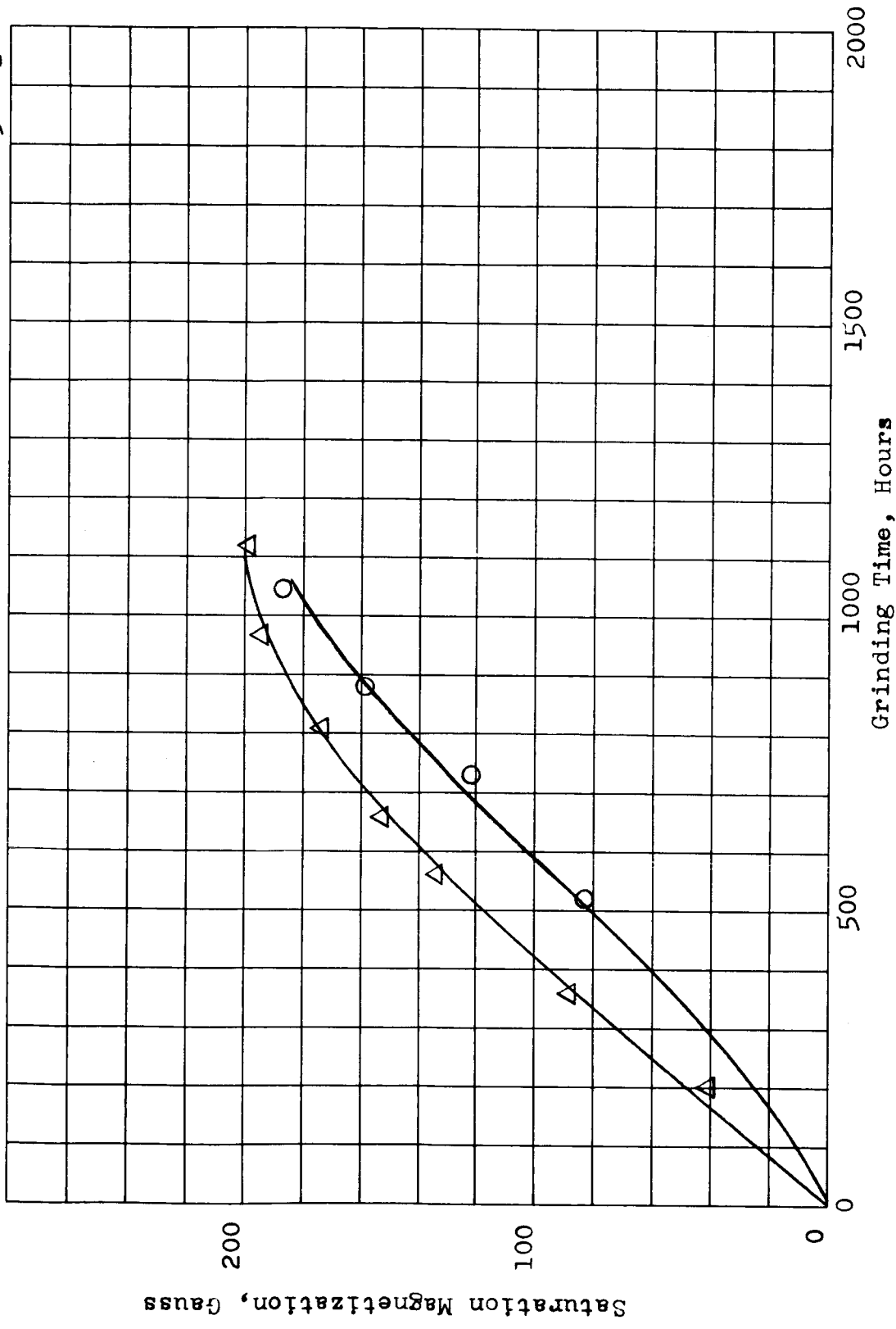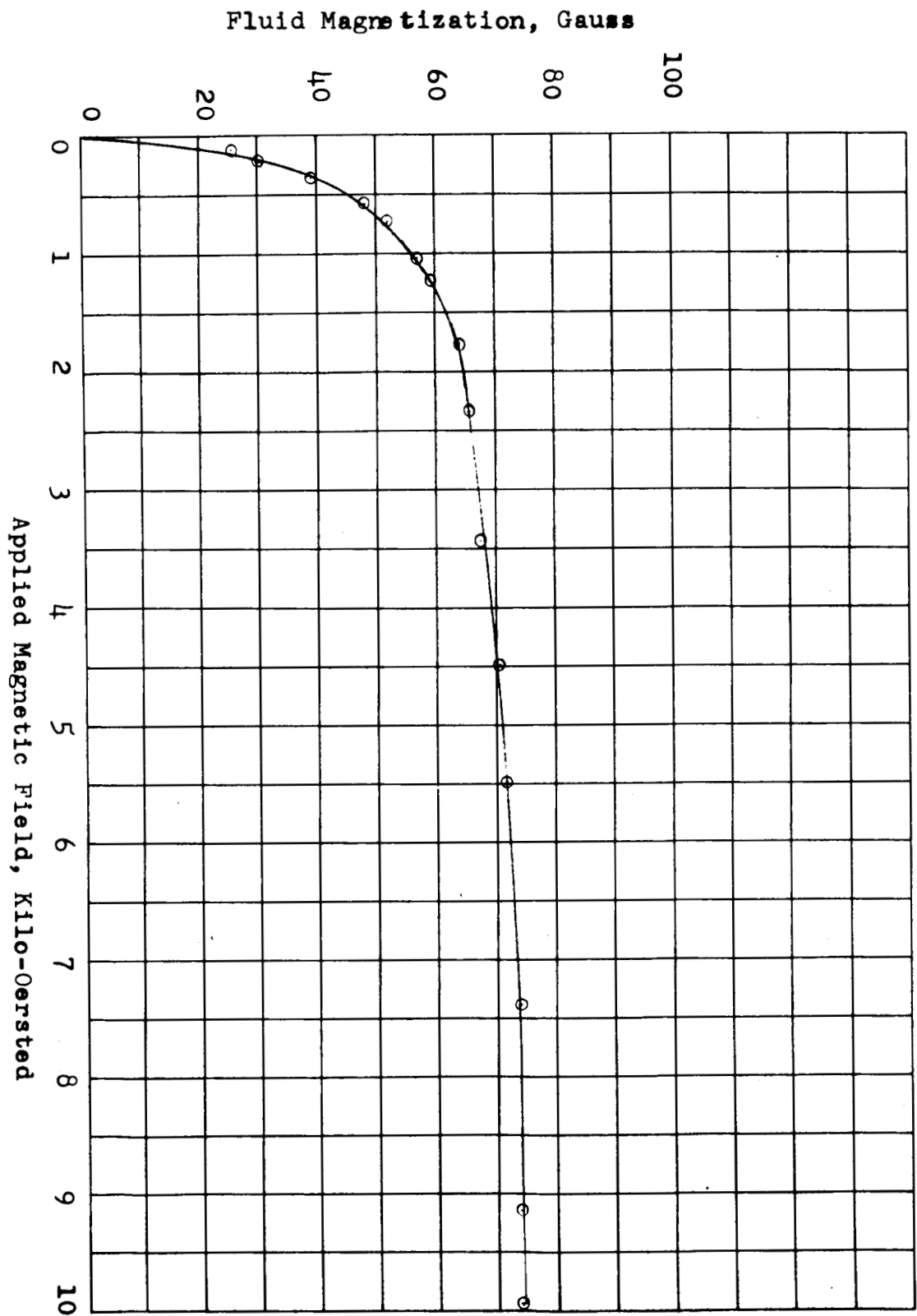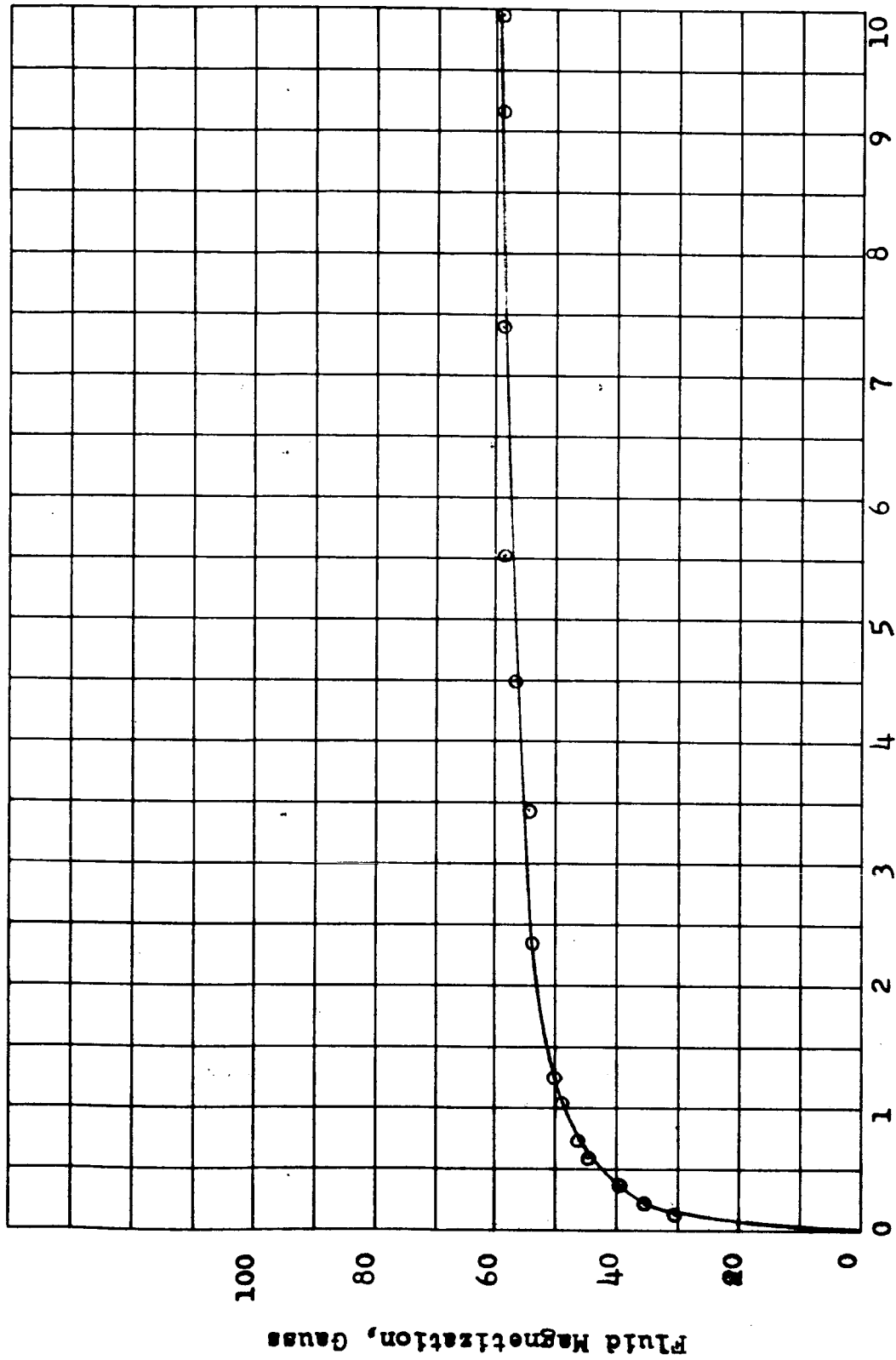
Figure 4: Effect of Magnetite Concentration on the Formation of a Magnetic Colloid

Figure 5   Magnetization curve of Water Base Ferrofluid G 80-T

Figure 6   Magnetization Curve of Water Base Ferrofluid G 80-B

The viscosity 30°C was 2.0cp for G80T and 1.3cp for G80B.

The factors affecting the stability of these fluids are presently being examined. Electron micrographs of these fluids are being taken for particle size analysis. It is planned to obtain viscosity curves for these fluids in the immediate future. These results will be presented in a subsequent report.

E. Development of More Concentrated Suspensions

One of the principal goals of the program is to develop ferrofluids of increased magnetic strength without a marked increase in fluid viscosity. The magnetization of a fluid, M, is equal to the product of the volume concentration of the magnetic colloid in suspension, ϵ, times the magnetization of the pure magnetic powder, M_p .

$$M = \epsilon M_p$$

(1)

The viscosity of a ferrofluid η_s can be expressed in terms of the viscosity of the base solvent, η_o , and the total volume fraction solids in suspension ϕ which includes the magnetic core and a stabilizing layer of finite thickness δ .

The viscosity relation is as follows:

$$\frac{\eta_s}{\eta_o} = \frac{1}{\left(1 - \frac{\phi}{\phi_c}\right)^2}$$

(2)

where ϕ_c is a critical packing concentration at which the suspension becomes rigid, as $\phi \longrightarrow \phi_c$, $\eta_s \longrightarrow \infty$. As previously discussed (Reference 4) ϕ_c can be taken to be equal to 0.74.

ϕ, the total volume fraction solids, is related to ϵ, the volume fraction magnetic material by the following expression:

$$\phi = \epsilon \left(1 + \frac{\delta}{r}\right)^3$$

(3)

where r is the radius of the magnetic particles. This assumes the system to be equal sized spheres.

Substituting Equation 1 into Equation 3 one obtains the following relation between M and ϕ.

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$$\phi = \frac{M}{M_s}\left(1 + \frac{\delta}{r}\right)^3 \tag{4}$$

As $\phi \longrightarrow \phi_c$ M reaches a limiting value M_m which will be a function of the nature of the magnetic powder, the size of the particles and the thickness of the stabilizing layer. Figure 7 is a plot of M_m versus particle diameter for different values of δ, based on Equation 4. The vertical lines represent the limits of the range of the size of the particles normally found in ferrofluids. It is difficult to stabilize particles larger than 250 $\overset{o}{A}$ and difficult to prepare particles smaller than 40 $\overset{o}{A}$. The limiting magnetization increases with increasing particle size and decreasing thickness of stabilizing layer. As particle size decreases, the thickness of the stabilizing layer becomes more and more important. The maximum saturation magnetization of a magnetite ferrofluid, within the range of geometric parameters specified that could be achieved is represented by the upper right hand corner of the box, is 2,600 gauss. For a real fluid of finite viscosity, the magnetization level that could be achieved would be less since it would be necessary to dilute the ferrofluid with a small amount of carrier solvent. In order to reduce the ratio of η_s/η_o to 1000, it would be necessary to dilute the fluid by about 3%. This sets the limiting magnetization to about 2,500 gauss.

Viscosity and particle size measurements were made for three ferrofluids (G4,5,6, G21 and G44). Two of these were oleic acid stabilized materials and one was a Tenlo 70 stabilized material. The three experimental plotted in Figure 7 represent the magnetization of the different fluids on the verge of their becoming solid at room temperature against the length-average particle diameter calculated from electron micrographs. The values of the saturation magnetization are corrected for the presence of non-magnetic impurities. According to this limited information, the thickness of the stabilizing layer in oleic acid systems is about 40 $\overset{o}{A}$ while it is slightly higher than 20 $\overset{o}{A}$ for the Tenlo 70 system. By increasing the size of the particles in the system, with oleic acid the maximum saturation magnetization obtainable would be 1800 gauss. For Tenlo 70 stabilized systems, the limiting value would be 2500 gauss.

Figure 7 shows that great importance of particle size in developing fluids of higher strength. Since it is unlikely that a surfactant will be found that will result in a stabilizing layer thickness of less than 20 $\overset{o}{A}$ (even though a continuing effort will be made to do so), special attention will be made to developing Tenlo 70/kerosene base ferrofluids in which the particles are at least 150 $\overset{o}{A}$ in diameter. Such fluids should have a maximum saturation magnetization of at least 2000 gauss.
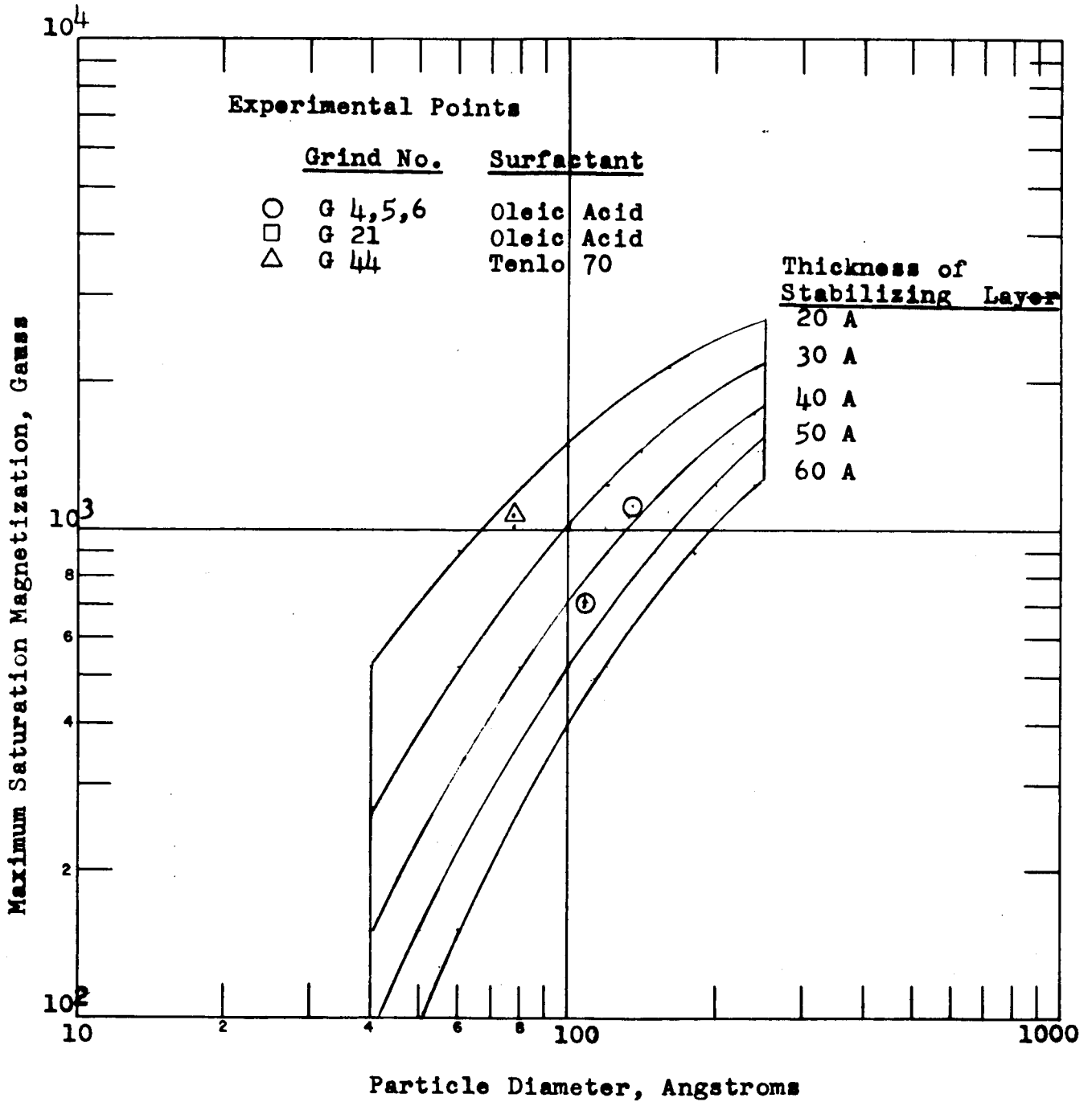
Figure 7 : Maximum Magnetization of a Ferrofluid as a
Function of Particle Geometry

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3) Duomeen L11 (G73): Duomeen L11 is a beta diamine marketed by Armour Industrial Chemical Co. This compound has the following formula:

$$CH_3-(CH_2)_9-CH-CH_3$$
$$|$$
$$H\cdot N-(CH_2)_3-NH_2$$
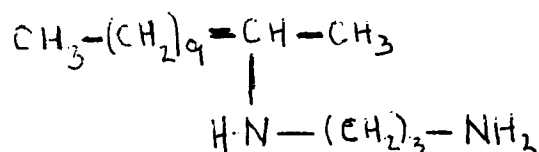
This saturated amine has two reactive groups which could interact with the particle surface, a primary and secondary amine. Unfortunately this compound behaved in an analogous manner to the straight chain amines, definite but negligible ferrofluid formation.

The conclusions drawn from the above experiments is that saturated aliphatic amines are poor grinding agents for the formation hydrocarbon base magnetic colloids. Yet it was observed that these compounds proved to be effective dispersing agents in preliminary sedimentation tests, so that there must have been some interaction between the surfactant and the particle surface. Previous experiments with saturated and unsaturated C_{18} fatty acids, namely stearic acid and oleic acid have shown oleic acid to be an effective grinding aid, while stearic acid did not result in the formation of a colloid. This indicates that possibly an unsaturated fatty amine e.g. oleyl amine might prove to be a satisfactory dispersant. If this were the case, it would be a clear indication that the geometry of the molecule is of paramount importance in the formation of a stabizing layer around the individual particles. Results with very closely related fatty acids of differing degrees of unsaturation already tend to imply this (see next section).

b) Carboxylic Acids: Further work was carried with carboxylic acids of different molecular configuration. Cinnamic acid, an unsaturated aromatic acid was not a successful grinding agent for magnetite in an aromatic solvent, tetrahydronaphthalene (G69). This is considered due to the fact that this molecule was too short.

Myristic acid (G68) which is a saturated fatty acid with a fourteen carbon chain did not form a stable colloid in kerosene. A commercial linseed oil fatty acid mixture (Wochem 441) (G63) formed a stable colloid. The principal component of this mixture is linolenic acid

$$CH_3(CH_2CH=CH)_3(CH_2)_7COOH$$
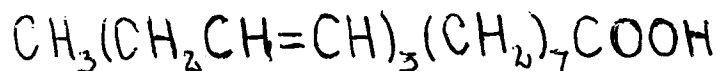
an unconjugated triply unsaturated fatty acid. A commercial chinawood fatty acid mixture (Wochem 400)(G61) on the other hand, only formed a gel which when broken did not form a magnetically responsive colloid. The main component of this mixture is eleostearic acid:

$$CH_3(CH_2)_3(CH=CH)_3(CH_2)_7COOH$$
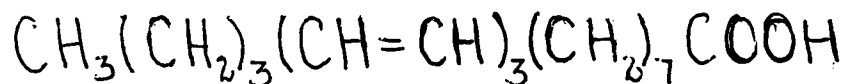
which differs from linolenic acid in structure only in the position of the double bonds. It should be noted that in phase I of the program, it was found that stearic acid (saturated);

$$CH_3(CH_2)_{16}COOH$$
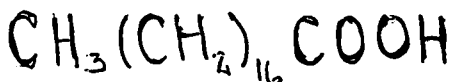
did not form a stable colloid but that oleic acid (singly unsaturated);

$$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$$
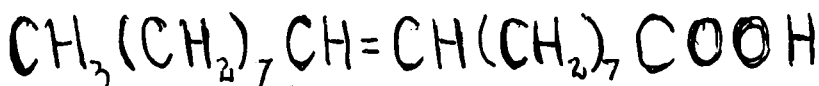
and linoleic acid (doubly unsaturated):

$$CH_3(CH_2)_3(CH_2-CH=CH)_2(CH_2)_7COOH$$
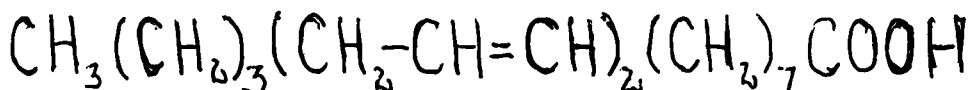
did form stable ferrofluids.

The results can only be explained in terms of varying degrees of rigidity of the molecule which effect the interaction of the organic tail of the adsorbed molecules with solvent molecules since variations in the adsorptivity of the carboxylic acid group should not change. The implications are that a very flexible molecule (stearic acid) or a very rigid molecule (eleostearic acid) do not form a solvated layer which would properly sheath the particles, whereas molecules of intermediate rigidity do (oleic acid, linoleic acid and linolenic acid).

The run was also made with unsaponified linseed oil (G65). This is the glyceryl ester of the fatty acids used in run (G63). In this run the fatty acid groups were esterified to glycerol and were thus blocked. This run formed a viscous liquid but did not result in the formation of a magnetic colloid after 2000 hrs. of grinding. This implies the need for groups that can adsorb on the particle surface.

c. High Temperature Fluids: Grinds (G61) and (G63) were also carried out in order to prepare a raw material for the "overshoe" program, the preparation of thermally stable organic ferrofluids.

An alternate method of preparing a thermally stable ferrofluid would be to grind in the presence of stabilizing agents that do not absorb at elevated temperatures. High temperature dispersants have been developed by the petroleum industry as additives to automotive lubricating oils. Finely divided lead oxide and carbon particles are by-products of the combustion of leaded gasolines in an automotive engines. These particles are removed from the cylinders by the lubricating oil which circulates and are maintained in suspension by specially developed additives. A number of petroleum companies were contacted with little success since the