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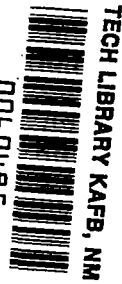NASA CR-1407
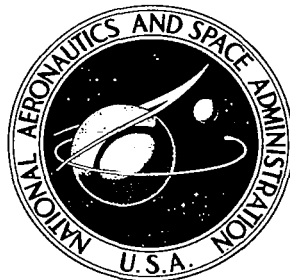
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STUDY OF FERROMAGNETIC LIQUID

by Robert Kaiser and Ronald E. Rosensweig

NASA CR-1407

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ABSTRACT

As reported in NASA CR 91684, it is possible to induce substantial
magnetic forces in ferrofluids. These are stable micro-dispersions formed
by grinding a ferromagnetic powder in the presence of a surfactant
solution. Novel hydrocarbon base ferrofluids with increased magnetization
(850 gauss at 10^4 oe) and improved thermal stability ($500^{O}F$ in a sealed
vessel) have been prepared. Water, fluorocarbon and non-volatile ester
base ferrofluids have also been synthesized.

Physical properties of numerous magnetite base ferrofluids were
measured. For these systems the particle size is less than 150 $\overset{o}{A}$. Magnetic
properties can be accounted for by superparamagnetic theory and particle
concentration. The maximum attainable concentration of particles varies
as a function of δ/D, the ratio of the stabilizing layer thickness to
the particle diameter. A minimum value of $\delta = 30$ $\overset{o}{A}$ was observed. Ferro-
fluid viscosity increases as a function of carrier liquid viscosity, particle
concentration and δ/D.   The dimensionless ratio of the viscosity of a
ferrofluid in a magnetic field to its viscosity in a zero field is a
function of $\dfrac{\gamma\, \eta_o}{MH}$, the ratio of hydrodynamic stress to magnetic stress,
and of δ/D.

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SUMMARY

        In the absence of a true ferromagnetic fluid, magnetic body and
surface forces of substantial magnitude can be induced in a liquid by
stably suspending sub-domain ferromagnetic particles in this liquid. The
association between the colloidal particles and the carrier liquid is
such that there is no bulk separation of the solid and liquid phases even
in the presence of an applied magnetic field. Papell of NASA Lewis
Research Center (ref. 1) originally discovered that grinding a coarse
magnetite powder in the presence of a heptane solution of oleic acid in a
ball mill resulted in the formation of a stable magnetic colloid. Since
that time, there has been an active interest in ferrofluids as these magnet-
ically responsive dispersions are called. Much of the basic research work
has been performed at Avco under the auspices of NASA/OART. As reported in
a previous contractor's report, the synthesis of ferrofluids by grinding
and their properties was studied in some detail and a general theory of
ferrohydrodynamic flow was postulated (ref. 7). This report describes
further work that has resulted in the preparation of ferrofluids of
improved physical properties.

        The synthesis of magnetically responsive colloidal dispersions (ferro-
fluids) by wet grinding in ball mills was further examined. Sixty experi-
mental grinding runs were performed during the course of the program. The
effect of the following parameters on the formation of a ferrofluid were
examined: the compositon of a magnetic solid, the nature of the carrier
liquid, stabilizing agent structure and concentration and equipment
variables.

        Dispersed magnetite ferrofluids were prepared in a widely varying
carrier fluid such as aliphatic hydrocarbons (kerosene), fluorocarbons
(Freon E-3 and Krytox oils), water, ethylene glycol, glycerol and esters
(dinonyl phthalate).

        The effectiveness of a surfactant on the formation of a ferrofluid
depends both on the nature of the polar group which interacts with the
particle surface and on the structure of the balance of the molecule which
interacts with the solvent. In hydrocarbon systems, for the surfactants
whose structure was well defined, carboxylic acid and hydroxyl terminated
surfactants resulted in the formation of a ferrofluid. Amine terminated
systems had little effect. Of the carboxylic acid and hydroxyl surf-
actants, only those molecules that contained one or two double bonds or a
benzene ring in the structure and were at least 18 $\overset{o}{A}$ long resulted in
ferrofluid formation.

        The maximum size of the suspended particles depended on the nature
of the surfactant used. The thicker the stabilizing layer formed by the

surfactant in the carrier liquid, the larger was the size of the resulting particles at the end of the grind.

Prolonged grinding of the magnetic metals with a higher domain magnetization than magnetite did not result in the formation of a stable ferrofluid, even though there was evidence of substantial size reduction.

The successful grinding operations produced a raw material that could be subjected to any of a number of modification steps to produce a wide variety of ferrofluids with tailored properties.

Particle size distribution could be altered by high speed centrifugation and magnetic concentration. Magnetic concentration is applicable only to ferromagnetic suspensions and takes advantage of the increased magnetic response for superparamagnetic particles of larger size. Particle concentration could be increased by vacuum evaporation. Additional or alternate carrier fluid or surfactant could also be added to further modify the suspensions.

A number of novel ferrofluids were produced during the present program. These include:

    i.   Fluids of increased magnetization - By combining centrifuging and magnetic separation techniques, the magnetization of a 100 cp kerosene base ferrofluid was increased from 600 gauss to 735 gauss, which represents an increase of over 20%. Fluids with a magnetization of 850 gauss were also obtained; these had viscosities of 6600 cp.

    ii. Fluids with improved stability characteristics - A kerosene base ferrofluid stabilized by ENJAY 3854, a polybutene surfactant, proved to have much improved thermal properties. Samples of this ferrofluid in sealed ampoules survived prolonged exposure at 260°C and lower temperatures without any measurable effect on the properties of the suspension, but separated into two phases when heated to 315°C for 24 hours. All other ferrofluids tested were severely affected by exposure to temperatures greater than 150°C.

    iii. Fluids with different carriers - Ferrofluids prepared with water and fluorocarbon as the carrier liquid have different physical properties than the hydrocarbon ferrofluids prepared in the past. In particular, the immiscibility of fluorocarbons with both oil and water systems should make the ferrofluids prepared in Freon E-3 and Krytox oils extremely valuable.

iv. Fluids of low volatility - Stabilization of a
     suspension in dinonyl phthalate with Triton X45
     surfactant, an octyl phenol ethoxy adduct, and
     in Krytox AC fluorocarbon oil with a high
     molecular weight fluorocarbon surfactant, has
     resulted in ferrofluids of unusually low vapor
     pressure which have been exposed to the atmosphere
     at room temperature for extremely long periods
     of time without the risk of fluid evaporation.

The magnetic properties of the ferrofluids can be correlated by super-
paramagnetic theory in terms of the size distribution of the suspended
particles as obtained by electron microscopy, the domain saturation of the
particles and their volume concentration.

The flow properties of the ferrofluids, in the absence of an applied
magnetic field and interparticulate interaction, are solely a function of
the volume concentration of the solvated particles and of the viscosity of
the carrier fluid. The viscosity as a function of applied magnetic field
was measured for different ferrofluids. By using dimensional analysis, a
correlation for η_H, fluid viscosity in an applied field, was obtained in
terms of the ratio (η_H/η_s) as a function of the ratios $\gamma\eta_o/MH$ and δ/D,
assuming no particle interaction. In the above,

η_o = Carrier liquid viscosity, poise

η_s = Ferrofluid viscosity in the absence of a magnetic field, poise

D = Particle diameter, cm

δ = Thickness of stabilizing film around a particle, cm

γ = Shear rate, sec^{-1}

M = Magnetization of fluid, gauss

H = Applied magnetic field, oe

$\gamma\eta_o/MH$ is the ratio of hydrodynamic stress to magnetic stress. When
$\gamma\eta_o >> MH$, viscosity of the magnetic suspension is independent of δ/D
and (η_H/η_s) $\longrightarrow$ 1. When $\gamma\eta_o << MH$, viscosity of the suspension is
again independent of δ/D, but now (η_H/η_s) $\longrightarrow$ 4. For intermediate
values of $\gamma\eta_o/MH$, the ratio η_H/η_s becomes a function of δ/D and is
dependent on shear rate and magnetic field. Typically for a value of
δ/D = 0.35, the transition is characterized by $10^{-7} \leq \gamma\eta_o/MH \leq 10^{-5}$.

INTRODUCTION

It has been found that stable suspensions of very finely divided magnetic solids exhibit very unusual fluid mechanical properties in the presence of an applied magnetic field. At the present no true ferromagnetic fluid is physically known even though its existence is theoretically possible. The magnetic liquids that are the focus of these studies are stable micro-dispersions of sub-domain magnetic particles in a carrier liquid. The association between the colloidal particles and the carrier liquid in which they are suspended is such that there is no bulk separation of the solid and liquid phases even in the presence of an applied magnetic field. The ferrofluids, as these micro-dispersions are called, are the only liquid media known today in which it is possible to induce substantial magnetic body forces.

Ferrofluid technology is still in its infancy. The initial work done by Papell of the NASA Lewis Research Center on dilute magnetic dispersions in hydrocarbons was published in 1963 (ref. 1). This is the same time that E.L. Resler, Jr. of Cornell University and R.E. Rosensweig of Avco became interested in a ferromagnetically responsive liquid in order to develop an efficient magnetocaloric energy conversion cycle. Since then, a continuous and increasing effort has been devoted to the study of the field of ferrohydrodynamics at Avco.

Initially in 1965, only a very weak oleic acid stabilized dispersion of magnetite in kerosene was available. The saturation magnetization of this fluid was less than 100 gauss. Today, fluids with a magnetization saturation approaching 1000 gauss are available with fluids of about twice this magnetization considered feasible. The limitations of kerosene base systems are obvious. Magnetic dispersions have since been prepared in many other media such as water, glycerol, some silicone oils, esters, etc. It is hoped to extend this list even more since most applications which use ferrofluids place unique requirements on the combination of the other physical properties of the fluid that is being used.

Concurrently with fluid development, and with the availability of a magnetic fluid, a number of physical phenomena have been discovered and observed for the first time. The initial discovery was the positioning of a magnetic fluid in space with a magnetic field by Papell (ref. 2). Avco discovered subsequent phenomena such as the buoyancy of non-magnetic and magnetic objects in a ferrofluid (ref. 3), the magnetocaloric power cycle (ref. 4), the formation of "liquid spikes", spontaneously formed instabilities of a magnetic fluid interface in the presence of a normally applied field (ref. 5), and the rotation of the fluid induced by time varying magnetic fields (ref. 6).

The theory underlying the field of ferrohydrodynamics was developed and advanced by Avco in order to obtain a better understanding of the

observed physical phenomena. Initially, it was found that a modified Bernoulli equation could take into account the effects of magnetic body forces (ref. 3). With the discovery of "liquid spikes", which could not then be explained, a more exact tensorial analysis was developed which was able to account for this phenomenon as well as the other discoveries made (ref. 6).

The basic research and development on fluids has led to a number of practical uses and inventions in a wide variety of fields. These include the positioning of rocket motor fuel in a zero "g" environment, novel pumps and other energy conversion devices, viscous dampers for gravity gradient satellites, accelerometers, instrument support bearings, specific gravity analyzers, seals, etc. Ferrofluids are also finding utilization in the medical field as a method of sealing cranial aneurysms, transporting a liquid within the body without recourse to surgery and as a driving medium for a unique heart assist pump.

A previous report, (ref. 7) documents the synthesis and properties of ferrofluids prepared by grinding and the discoveries of the phenomena of buoyant levitation and the formation of "liquid spikes". The grinding mechanism was studied in some detail in order to obtain a better understanding of dispersions in non-aqueous media. Theoretical studies leading to a generalized theory of ferrohydrodynamic flow which took into account the formation of "liquid spikes" were also presented in this report.

The present report discusses results obtained under a continuation program. The principal goals of this phase of the study were to:

1. Improve the magnetic properties of the ferrofluids,

2. Prepare samples for testing of fluids in a variety of carrier liquids,

3. Improve the thermal stability of the ferrofluids,

4. Measure the principal physical properties of the sample ferrofluids,

5. Correlate the experimental results and observations in terms of physico-mathematical models.

The measurements of fluid viscosity in high magnetic fields were performed in one of the high field solenoids unique to the Francis Bitter National Magnet Laboratory at M.I.T. while Robert Kaiser was a guest scientist. These measurements could not have otherwise been performed.

The modifications of the viscosimeter required by these high field measurements were performed by the Brookfield Engineering Laboratory of Stoughton, Mass.

In addition to the authors, the following members of the Avco staff also contributed to the program:

Mr. Gabor Miskolcsy who carried out the dielectric measurement studies and participated in the viscometry at high magnetic fields.

Mr. John Zurbrick who provided the dielectric probe and suggested the experimental approach that was followed.

Mr. Paul Burnett and Mr. Charles Houck who took the electron micrographs necessary to this work.

Dr. Robert Haag and Mr. Philip Berneburg who carried out the x-ray diffraction work.

Mr. Samuel Barchus and Mr. Peter Malatesta who were of great assistance throughout the experimental program.

PREPARATION OF FERROFLUIDS

Stability Considerations

Before describing the method of preparation of the ferrofluids, it is useful to review the factors which control the stability of ferrofluids and the requirements these stability considerations place on the structure of a ferrofluid. A detailed discussion of particle interactions and system stability has been published (ref. 8).

In addition to the energy associated with London forces of inter-particle attraction, E_L, which exist in any colloidal system, in a ferrofluid there is an additional energy due magnetic force of attraction, E_M, between the sub-domain particles in suspension. Both these forces vary with increasing particle diameter, D, and relative surface separation, h, where

$$h = 2 \left(\frac{b}{D} - 1 \right) \qquad (1)$$

b = center to distance between the particles.

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In order to prevent agglomeration of particles as a result of these forces, the particles are made small enough so that at large values of h, thermal motion of the particles is large in comparison to $E_M + E_L$ and at the same time, the particles are coated with a stabilizing film of thickness, δ , which established a contact value of $h = \frac{4\delta}{D}$. Any further approach of the two particles is hindered by a mechanism of entropic repulsion, E_R, which takes into consideration the energy necessary to have inter-penetration of two molecular films. A criterion for stability is that the curve of potential-energy versus distance-of-separation for two particles must have a maximum considerably greater than kT and no potential wells deeper than kT. This can be expressed as follows:

For $0 \leq h \leq 4\delta/D$, there must exist a maximum

$$\frac{\partial[E_R - E_M - E_L]/kT}{\partial h} = 0 \qquad \text{(energy barrier)} \qquad (2)$$

where

$$\frac{E_R - E_M - E_L}{kT} \gg 1$$

For $h > 4\delta/D$, $E_R = 0$ and stability requires that

$$\frac{|E_M + E_L|}{kT} < 1 \qquad \begin{array}{l}\text{(absence of deep} \\ \text{potential well)}\end{array} \qquad (3)$$

Condition (3) implies that the total energy of attraction between two tangent solvated particles is less than the energy associated with thermal motion. Since E_M and E_L decrease with distance of separation, the most severe condition in this case exists when $h = 4\delta/D$. At this value of h, the following equations are obtained for E_M and E_L(ref. 8):

$$E_M = -\frac{M_d^2}{288}\left(\frac{D}{\frac{2\delta}{D}+1}\right)^3 \qquad (4)$$

where M_d = domain magnetization, and

$$E_L = \frac{-A}{12}\left[\frac{1}{\frac{4\delta}{D}\left(\frac{\delta}{D}+1\right)} + \frac{1}{\left(\frac{2\delta}{D}+1\right)^2} - 2\ln\frac{\frac{4\delta}{D}\left(\frac{\delta}{D}+1\right)}{\left(\frac{2\delta}{D}+1\right)^2}\right] \quad (5)$$

The term A is a dimensional quantity related to an optical dispersion frequency whose numerical magnitude has been found to be about 10^{-12} erg for many disperse oxide systems (ref. 9).

In Figure 1, the function, z, where

$$z = \frac{(E_M + E_L)}{kT}$$

for magnetite spheres is plotted as a function of δ and D. In this case, M_d = 5660 gauss, A = 10^{-12} ergs (assumed) and kT = 4.15 x 10^{-14} ergs. By (3), the value of z = 1 is taken as representative of the value that separates stable from unstable systems. When z > 1, it is possible for the particles to associate into chains and form a gel.

This figure shows the relative influence of E_L and E_M. E_L is a function of δ/D whereas E_M is a function of D as well. The flat regions of the curves for values of D < 40 Å correspond to domination of the attractive by E_L (E_L > E_M). The sharp increase in z for D > 40 Å corresponds to the domination of magnetic attractive forces (E_M > E_L).

This plot also shows that there is a minimum value of δ/D needed because of E_L requirements. This value is somewhat larger than 0.1. It also shows that as the particle size increases, the required ratio δ/D has to increase disproportionately to compensate for E_M. The values of M_M correspond to the saturation magnetization that would be obtained in a hexagonally close packed system of solvated spheres for the different values of δ/D.

Similar curves can be drawn for other magnetic solids. The curves for iron (M_d = 20,000 gauss) are shown in Figure 2. The same general behavior is noted except that E_M predominates at much smaller values of D. The size of the particles that are stabilized for a given value of δ/D are smaller by about a factor of two. Magnetically stronger fluids are theoretically possible with iron than with magnetite because of higher domain magnetization, but the required particle is much smaller.

For a given magnetic material, the limiting value of M_M is defined by the ratio δ/D at a value of z = 1. Empirically, it appears as though the minimum attainable value of $\delta \simeq 20$ Å (ref. 8). With this value of from Figure 1 it appears as though magnetite base fluids could theoretically attain a saturation magnetization of about 1500 gauss and iron base fluids of about 3000 gauss.

The above values bound the goals of the experimental program described in subsequent sections.

Synthesis of Ferrofluids

Introduction. - Ferrofluids are prepared by Avco by prolonged wet grinding.
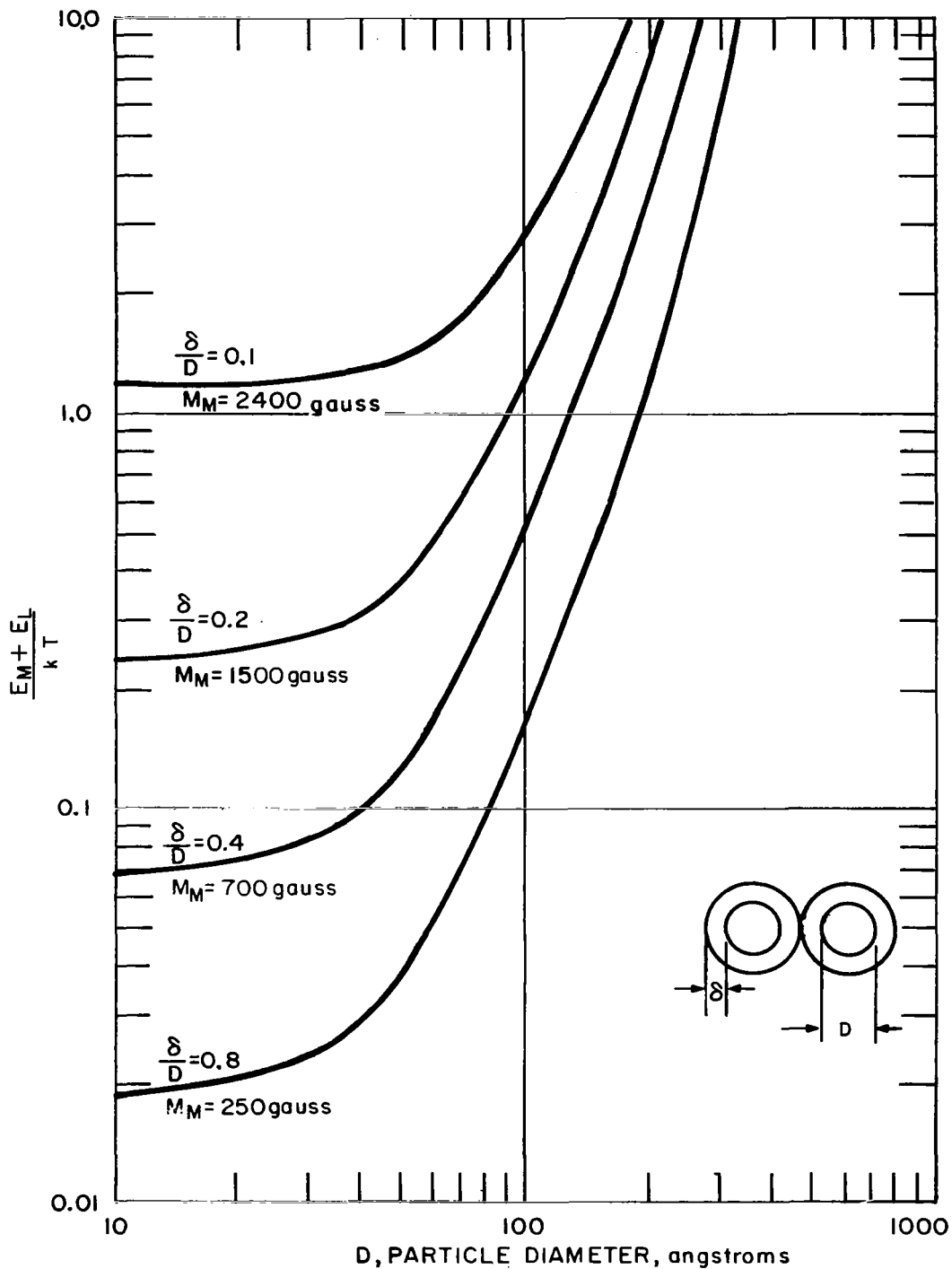
Figure 1 POTENTIAL ENERGY OF TANGENT SOLVATED SPHERICAL MAGNETITE
PARTICLES AS A FUNCTION OF PARTICLE DIAMETER D AND
STABILIZING LAYER THICKNESS

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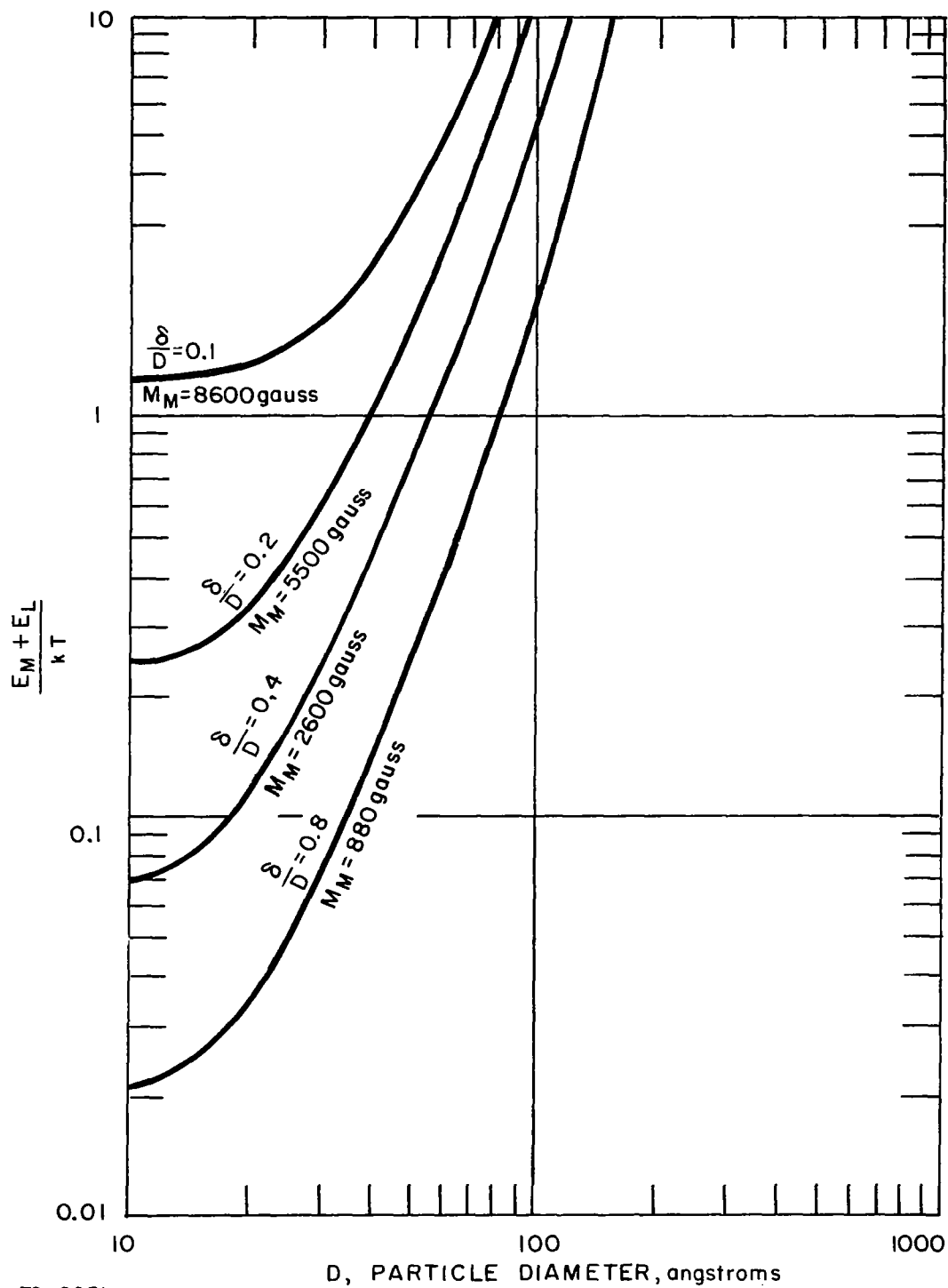
Figure 2 POTENTIAL ENERGY OF TANGENT SOLVATED IRON PARTICLES
(M_d = 20,000 GAUSS) AS A FUNCTION OF PARTICLE DIAMETER
D AND STABILIZING LAYER THICKNESS

The grinding experiments consist in placing a mixture of magnetic powder, carrier liquid and surface active agent in a ball mill half-filled with steel balls. The grinding equipment used and the standard composition of the charges are listed in Table 1. The mill is then rotated axially for an extended period of time. Periodically, the contents of a mill are examined. The sample is centrifuged and the density, ρ, and magnetization in both high and low applied fields, M_L and M_H, of the supernatant liquid is measured. The density and high field magnetization are indices of the volumetric concentration of magnetic solid particles in suspension while the ratio M_L/M_H is an index of the size of the particles in suspension (see magnetic properties section). These experiments have been previously described in detail (ref. 7). The only additional information that was obtained during this phase of the program was the ratio M_L/M_H.

Table 1 - GRINDING EQUIPMENT AND STANDARD COMPOSITION OF CHARGES

Ball Mill Capacity	Ball Size Inches	Carrier Liquid, cc	Surfactant, cc	Magnetic Powder, cc
2.0 pint	1/8 - 1/4	300	30	10
4.7 pint	1/4 - 1/2	625	50	20
1.6/2.0 gal.	1/4 - 1/2	1250	100	40
3.0 gal.	1/4 - 1/2	3750	300	120
27 gal.	1/2	27000	2200	880
Ball Load = 50% of mill volume				

Over sixty grinding runs were initiated during the course of the program. The major emphasis of the study was on finding surfactant/solvent combinations that would result in ferrofluids with novel properties. This included the preparation of water base, fluorocarbon base as well as improved hydrocarbon base ferrofluids. Attempts were also made to grind magnetic metal powders in the hope of developing stronger magnetic fluids.

General Results. - It is the grinding experiment that determines whether a stable ferrofluid is formed. An unsuccessful grinding run is characterized by separation of the solid and liquid phases in a gravitational or magnetic field or by the formation of an intractable gel that cannot be broken by further addition of either solvent or surfactant. A successful grinding run results in the formation of a dispersion of magnetic particles that is indefinitely stable under the influence of gravity or magnetic field gradients. There is no separation of the solid phase from the carrier liquid.

There is a progressive increase in density and high field magnetization of the fluid with time. These are both functions of the volumetric concentration of colloidal magnetite in suspension. As discussed in a

previous report (ref. 10), the rate of colloid formation is represented by sequential first-order kinetic steps of break up and can be expressed by the following equation:

$$Z = 1 - e^{-K_1 t} (1 + K_1 t) \qquad (6)$$

where Z is the fractional conversion of colloidal in the system at time t, and K_1, a characteristic rate constant for the system.

The above is an expression for the total fraction of material below a certain arbitrary size, D_c, as a function of time without actually considering the particle size distribution below the arbitrary diameter. The value of the ratio of the low field magnetization to the high field magnetization, M_L/M_H is a measure of the size distribution of the particles of diameter $D < D_c$. It was found that the ration, M_L/M_H was invariant with time during a grinding operation.

This finding is in accord with the cascade mechanism originally proposed for the formation of colloidal particles which suggested that the colloidal particles detected were formed by attrition of an intermediate sized parent particle. It suggests that the colloid producing particles break down in a characteristic manner which gives birth to daughter particles in the colloidal range with a fixed particle distribution. This finding also implies that once the particles are in suspension they are no longer affected by the grinding action of the balls. The size distribution is determined not by the length of time of the grind but is pre-ordained by the composition of the grinding mixture, the carrier liquid, stabilizing agent and magnetic powder.

The specific results obtained for the various grinding runs performed are discussed in subsequent sections in the following order:

1) Preparation of ferrofluids in other carrier liquids than hydrocarbons,

2) Preparation of ferrofluids with magnetic solids that have a higher saturation magnetization than magnetite,

3) Preparation of improved hydrocarbon base ferrofluids with novel stabilizing agents,

4) Process studies with hydrocarbon base ferrofluids.

Post-Grinding Modification of the Ferrofluids

Given a certain suspension, modification involves operations which alter the size distribution, concentration and ratio to other constituents, of the suspended particles as well as the nature of the suspending medium.

A standard operation performed on a ferrofluid subsequent to grinding after a successful run was centrifugation at 17000 g for 10 minutes to remove oversized particles nominally larger than 350 Å. This basic raw material could be modified a number of ways: altering the concentration of the magnetic sol by dilution or vacuum evaporation, flocculation/redispersion or solvent exchange to alter the carrier solvent, extensive centrifugation or magnetic gradient diffusion to alter the particle size distribution, etc. Except for the last named operation, all these methods were already described.

Magnetic gradient diffusion method is of special interest since it is only applicable to ferrofluids. The basic properties of a ferrofluid rely on the fact that there is no gross separation of the magnetic particles from the carrier liquid in the presence of a magnetic field. However, a particle concentration gradient should occur in the presence of a magnetic field gradient. It is of interest to examine the prediction of theory regarding this segregation phenomenon. From statistical mechanics the distribution of particle concentration at equilibrium obeys the following relationship

$$n = C \, e^{-U/kT}$$

where n is particles/cm^3, U is energy per particle, k is the Boltzman constant, T absolute temperature, and C a constant. If a particle is unaffected by the presence of other particles and only magnetic forces are present then

$$U = -pH$$

where H is the magnetic field and p is the magnetic moment per particle.

$$p = \frac{1}{4\pi} \cdot \frac{\pi D^3}{6} \cdot M_d$$

$$= \frac{D^3 M_d}{24}$$

For a mono-dispersed system, n is directly proportional to saturation magnetization of the local fluid sample M_s. Thus the ratio of magnetization at two points from the foregoing is given by

$$\frac{M_{s1}}{M_{s2}} = \exp \left(\frac{D^3 M_d (H_1 - H_2)}{24 \, kT} \right) \tag{7}$$

or, solving for the particle diameter,

$$D = \left(\frac{24 \, kT}{M_d (H_1 - H_2)} \ln \frac{M_{s1}}{M_{s2}} \right)^{1/3}$$

This tendency for magnetic particles to diffuse in a magnetic field gradient is a strong function of particle diameter, as shown in Figure 3. It is limited by geometrical hinderance due to close packing of particles.

The magnetic equivalent of Stokes law for the sedimentation rate of a solvated magnetic particle in a field gradient dH/dY is expressed by the following equation:

$$S_M = \left(\frac{D^2}{18 \, \eta_o \, (1 + \frac{2 \delta}{D})} \right) \left(\frac{M_d}{4 \pi} \right) \left(\frac{dH}{dY} \right) \tag{8}$$

S_M = rate of particle sedimentation due to magnetic forces

η_o = solvent viscosity, poise.

It is similar to the classical equation for the sedimentation rate, S_g, of a particle under acceleration forces:

$$S_g = \frac{D^2 \, a \, (\rho_c - \rho_o)}{18 \, \eta_o \, (1 + 2 \, \delta/D)} \tag{9}$$

where   a = applied acceleration

ρ_c = core particle density

ρ_o = carrier liquid density = solvated layer density.

In both cases the sedimentation rates vary as $\frac{D^2}{(1 + \frac{2\delta}{D})}$.

Equal sedimentation rates will be obtained with a saturated magnetite particle suspended in a unit density fluid subjected to either an acceleration of 1 g (981 cm/sec^2) or 9 oe/cm according to the above equations. However, magnetic diffusion offers two advantages over centrifugal techniques:

1. The equipment for magnetic diffusion requires no moving parts; the fluid remains quiescent in a magnetic field. This permits experiments which can last as long as one wishes. High speed centrifugation requires rapidly rotating machinery so that experiments are of a short term duration.

2. Magnetic diffusion differentiates between magnetic and non-magnetic particles whereas centrifugation does not.
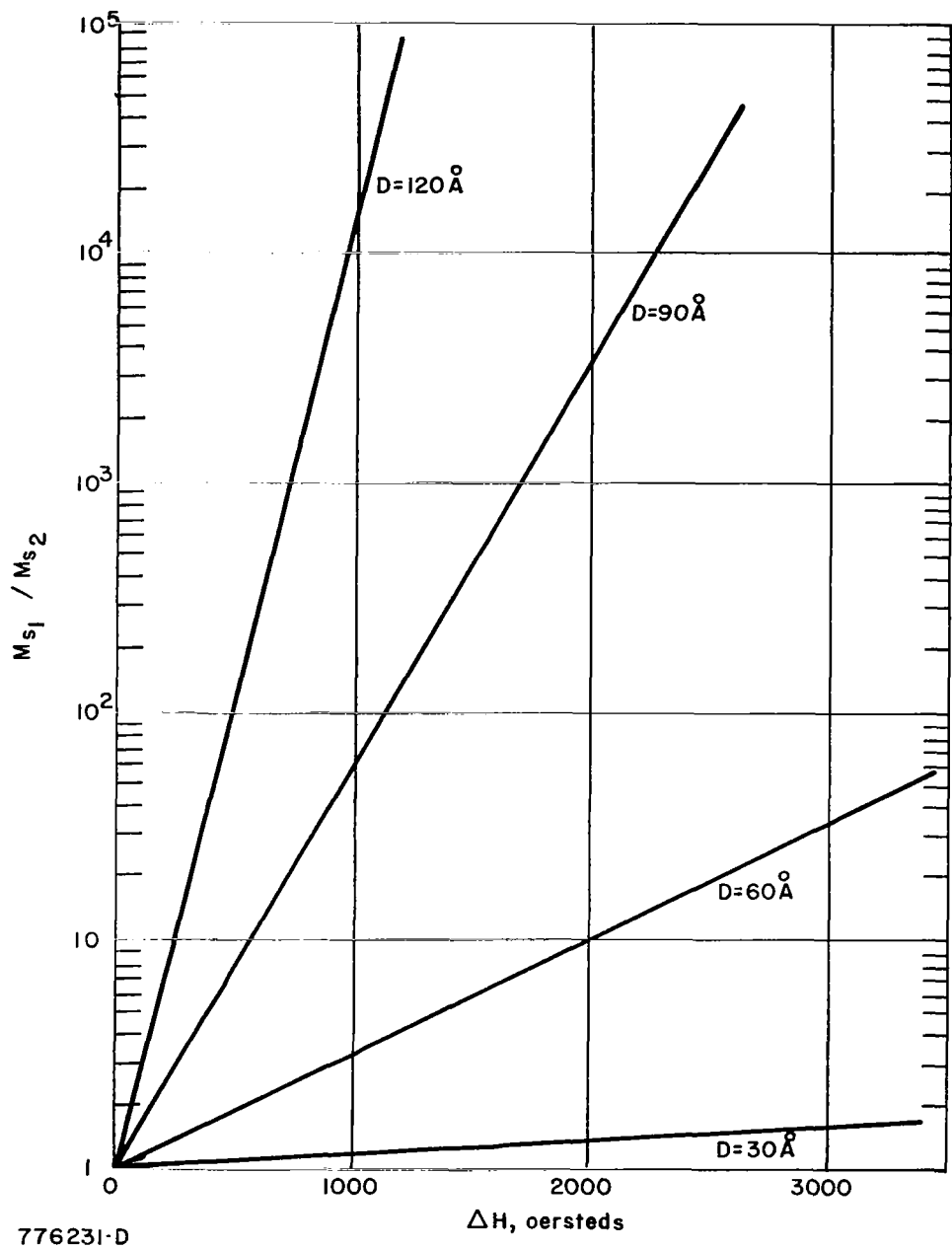
Figure 3 EQUILIBRIUM MAGNETIC PARTICLE CONCENTRATION INHOMOGENEITY
IN A MAGNETIC FIELD DIFFERENCE AS A FUNCTION OF
PARTICLE SIZE AT 300°K

776231-D

The experimental technique is very simple. Preliminary experiments were with a C-shape permanent magnet, the pole pieces of which define a magnetic gap in which the magnetic flux is rather uniform. Outside of this region the field has steep gradients. Finally, sufficiently far away, the field is very low. Thus, the experiments consist in immersing the magnet into a pool of ferrofluid or placing part of a container of ferrofluid in the gap of the magnet, allowing the system to remain quiescent for a given period of time and finally separating the fluid in the gap from the surrounding fluid. To prevent evaporation, the apparatus was usually placed in sealed dessicator jars. In the experiments used, magnets had a gap flux of about 2000 oe and maximum gradients of the order of 1000 oe/cm.

Subsequent separations were carried out in a specially constructed magnetic dialysis cell that fitted between the circular pole pieces of an electromagnet, as shown in Figure 4. This arrangement offered numerous advantages in that

    1.   the magnetic fields have circular symmetry;

    2.   higher magnetic field gradients can be generated;

    3.   the magnetic field gradient can be controlled; and,

    4.   separation of different fluid cuts from the outer wall of the device in towards the center is easily accomplished by reducing the magnetic field generating current.

In a typical run, a 400 cm^3 sample of fluid is subjected to an average gradient of 2000 oe/cm for a period of at least 24 hours. At the end of the run, the fluid is separated into a number of cuts, usually at least three: the least magnetic fluid from the outer periphery which drains under the influence of gravity at a high current setting, a second cut obtained when the current to the electromagnet is lowered to an intermediate value and a core cut obtained when the electromagnet is shut off. By systematically repeating the dialysis process, it is possible to selectively concentrate particles of a given size.

Repeated dialysis was carried out on one grind product in order to prepare a more magnetic ferrofluid. In these experiments, a ferrofluid was subjected to dialysis. The combined gap product (Stage 1) from thirteen parallel experiments was dialyzed in turn in three separate experiments. The combined gap product from these experiments (Stage 2) were further dialyzed to yield a third stage product. These experiments are summarized in Table 2. As can be seen from Figure 15, sequential dialysis results in a systematic improvement in the magnetization character- istics of a ferrofluid. At constant viscosity, the magnetization of the fluid increases by about equal increments per stage. The third stage

FILL

NON MAGNETIC
HOLDER

FLUID CAVITY

POLE PIECE

POLE PIECE

4 1/2"
DIA

7/8"

DRAIN
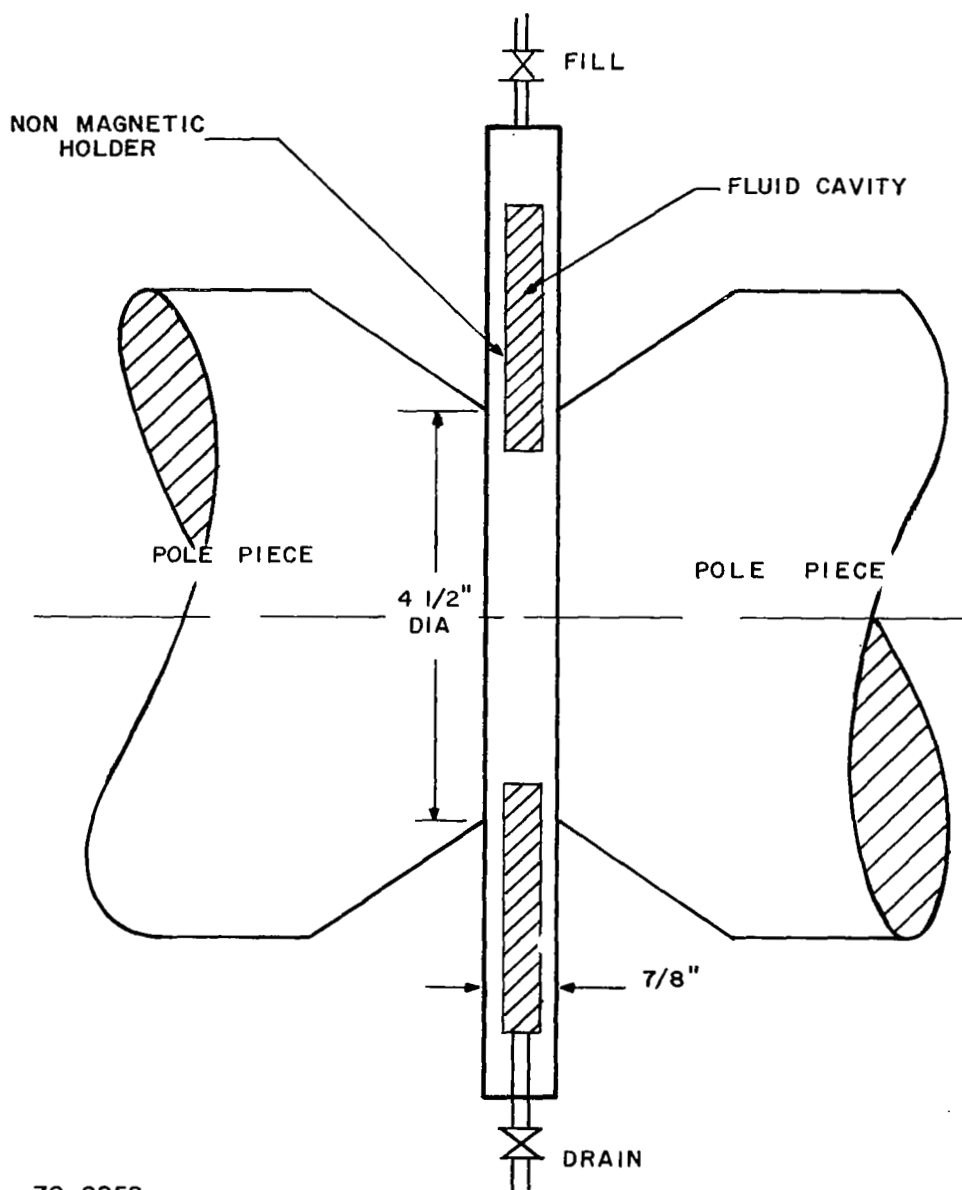
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Figure 4 SKETCH OF MAGNETIC DIALYSIS CELL

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product had a saturation magnetization of 850 gauss with a viscosity of 10^4 cp. These results are discussed in the viscosity section in more detail. Further improvements would be expected from further staging which time did not permit to be carried out due to the greatly increased number of experiments that would be required (about fifty).

Table 2 - MAGNETIC DIALYSIS EXPERIMENTS

Test Conditions			
STAGE	1	2	3
Number of Experiments	13	3	3
Cell Volume, cm^3	400	155	155
Average Test Duration, hrs.	24	64	64
Magnetic Field Gradient, Kilo oe/cm	1.9	2.9	2.9
Gap Liquid Product, cm^3	90	95	95
Liquid Properties			
FEED TO:	Stage 1	Stage 2	Stage 3	-
PRODUCT FROM	-	Stage 1	Stage 2	Stage 3
MAGNETIZATION, gauss				
@ H = 116 oe, M_L	22	31	59	98
@ H = 10^4 oe, M_H	110	133	202	290
Density, gr/cm^3	0.918	0.947	1.035	1.106
Volume Percent Solids, ϵ_D	2.82	3.50.	5.50	7.05
Conversion K, %	68.3	67.2	65.0	72.0

Water Base Fluids

Ferrofluids prepared in the past have been oil base, water immiscible systems. For many applications, there is need for water soluble or water compatible fluids since water is such a universal solvent.

The same general technique that was used to prepare organic base ferrofluids was used in the grinding of a magnetic powder in the presence of the carrier liquid, now distilled water, in the presence of a stabilizing agent. Magnetite was the magnetic solid of choice since it is already in an oxidized state and is stable in aqueous media. The principal difference in the preparation of a water base ferrofluid was in the choice of stabilizing agents required. Since water is an ionizable liquid with a high dielectric constant, in addition to the stabilization mechanism of entropic repulsion, it is also possible to consider the development of electrostatic forces of repulsion.

Proper dispersion of solid particles in the 0.1 μ to 10 μ is critical in many industrial applications such as paints, for example, so that many numerous products have been prepared for that purpose. These include low molecular weight poly-electrolytes as the sodium salts of polyphosphoric acids and polymeric aryl alkyl sulfuric acids, some proteins, fatty acid soaps, etc. A difficulty is that a great deal of specificity exists in the adsorption of dispersants on solids so that good performance by a particular dispersant with one solid does not presume similar effectiveness with another (ref. 11). An additional difficulty in the present application is the tendency for most of these dispersant solutions in water at high concentrations to foam under conditions of violent agitation. This would interfere with the formation and utility of a ferrofluid.

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 of organic and inorganic pigments.

b. Tamol 850 (Rohm and Hass Co.). This is also sodium salt of a carboxylated polyelectrolyte, of longer chain length than Tamol 731, that is used as 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 sulfonate. 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.

In addition to these polymeric agents, the following outer dispersants were tried:

e. Triton X-100 (Rohm and Hass Co.). This is a water soluble iso-octyl phenoxy ethanol containing 10 moles of ethylene oxide. It is a common emulsifier and wetting agent.

f. Neodol 25-F (Shell Chemical Co.). This is a water soluble ethoxylated adduct of C_{12} to C_{15} mixture of primary alcohols and contains an average of seven moles of ethylene oxide per mole alcohol. It has found use as a heavy-duty controlled foaming detergent in industrial areas such as metal cleaning.

g. Aerosol C-61 (American Cyanamid Co.). This cationic surface active agent is a mixture of octadecyl amine and octadecyl guanidine salts of octadecyl carbamic acid reacted with ethylene oxide. It has found wide use as a dispersing agent.

The above compounds were considered potential dispersing agents on the basis of available literature. It was not possible to run screening tests as was done with the hydrocarbon dispersions because the magnetite was readily wetted by water and no noticeable effect on settling time was observed.

The best results were obtained when Aerosol C-61 was used as a stabilizing agent. There were some difficulties at the start of the run due to excessive foaming which were corrected by the further addition of 50 ml of Aerosol C-61. The run was stopped at 837 hours.

The value of K_1 for run G104 based on the magnetization of the system at the start of the run, is 8×10^{-3} hrs^{-1}. This compares favorably with the values obtained with Tenlo 70/Kerosene ($K_1 = 4 \times 10^{-3}$ hrs^{-1}) and oleic acid/Kerosene (2.6×10^{-3} hrs-1) in similar equipment (ref. 10).

The first water base ferrofluid was made using Tamol 731 as a stabilizing agent. Although very encouraging results were obtained, initially some difficulties were subsequently encountered.

Tamol 731 proved to be an initially effective dispersing agent if present in sufficient enough quantity. In all runs where this material was used as the dispersant, there was an initial formation of magnetic colloid (G70, G74, G80, G97). In all cases, there was an initial increase in colloid concentration with grinding time, up to a certain critical time. Further, grinding then results in flocculation of the previously stable system. This critical grinding time increases with increasing concentration of Tamol 731.

There is a problem of over-grinding in these Tamol 731/water systems which is different than the ones encountered in the kerosene base systems with monomeric stabilizers. In these systems a gel is usually formed which can be reversed by the addition of extra surfactant, the gel being due to an insufficient stabilizing layer. With Tamol 731 as the grinding agent for magnetite in water, at a given surfactant/magnetite ratio, further grinding or addition of further surfactant enhances flocculation. The unusual finding is the fact that the extent of grinding which takes place before flocculation increases with the initial concentration of stabilizing agent. A possible explanation for this phenomenon is that as long as there is an excess of surfactant in solution, there is little or no tendency for the polymeric surfactant to adhere to more than one particle. As new surface area is generated, the surfactant excess in solution decreases by adsorption of the molecules on the particle surface, until there is an insufficient amount left to coat the new surface generated. This surface could then interact with molecules already partially absorbed on other particles and would lead to a bridging of the particles, resulting in flocculation. Another explanation could be Van der Waals attraction forces between a coated and uncoated particle leading to irreversible flocculation.

Both Aerosol C-61 and Tamol 731 resulted in the formation of relatively coarse particles (see Table 5). It appears as though the stabilizing sheath in water systems is thicker than in hydrocarbon systems and thus can stabilize larger particles. Viscosity/magnetization data on Aerosol C-61 and even more so with Tamol 731 indicate a thicker stabilizing layer (see section on viscosity).

Both Aerosol C-61 and Tamol 731 stabilized water base fluids dispersed in glycerol. Only the Tamol 731 base material dispersed in ethylene glycol. This extends the list of useful carrier liquids. Addition of alcohol or acetone in both cases resulted in flocculation. Both these fluids were immiscible with hydrocarbon systems.

The other ionic stabilizing agents tried (Tamol 850, Blancol N, and Lomar D), did not result in the formation of a satisfactory product. 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.

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 (G108-110) were made with perfluoroctanoic acid as the stabilizing agent. In both cases there was no colloid formation. It was presumed that these runs failed because perfluoroctanoic acid was too short a molecule to provide stabilization in analogy with the findings that in hydrocarbon systems surfactants of at least twelve carbon atoms in length are needed to result in a successful colloid.

After extensive inquiries, it was found that E.I. DuPont de Nemours & Co. was developing some long chain fluorocarbon surfactants. These surfactants are prepared by the anionic polymerization of hexafluoro-propylene oxide (HFPO) which yields perfluoro-polyethers (of any desired chain length) that have an acyl end group. This acyl end group is then hydrolyzed to yield a long chain fluorinated molecule with a carboxylic acid terminal group that could be used as a stabilizing agent.

$$(n + 1) \ (CF_3 - CF - CF_2) \longrightarrow F(CF - CF_2 - O)n - CF - \overset{\overset{\textstyle O}{\|}}{CF}$$

$$O \qquad\qquad F- \qquad CF_3 \qquad\qquad CF_3$$

$$O \qquad + \ H_2O$$

$$HF + F(CF - CF_2 - O)n - CF - \overset{\overset{\textstyle O}{\|}}{C} - OH$$

$$CF_3 \qquad\qquad CF_3$$

The carboxylic acids are intermediates in the manufacture of a wide variety of fluorinated ethers sold by DuPont. Hydrogen or fluorine can be substituted for the carboxylic end group to yield products which have the following general formula

$$\overset{CF_3}{\underset{}{\big|}}\qquad\qquad \overset{CF_3}{\underset{}{\big|}}$$
$$F \ (CF - CF_2 - O)_n - C - A$$
$$\underset{F}{\big|}$$

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The lower molecular weight homologues (n $\leq$ 9) which are hydrogen end-capped (A = H) are sold as the Freon-E series of liquids. The higher molecular weight homologues (n > 9) which are completely fluorinated (A = F) are sold as the Krytox oils.

It was considered very likely that the similarity of structure of the surfactants and the inert liquids would result in ferrofluid formation for some specific surfactant/carrier liquid mixture. Furthermore, if a ferrofluid were formed, it would be possible to alter systematically the properties of either surfactant or carrier liquid and study the properties of the resulting colloids.

Experimental quantities of the following fluorocarbon surfactants were obtained:

1. HFPO Hexamer Acid (M.W. 1000)

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

where the first carbon bears a CF_3 group.
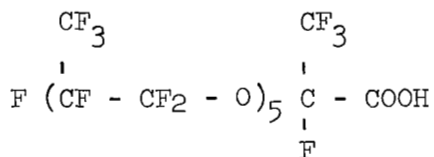
2. HFPO Decamer Acid (M.W. 1660)

$$F(CF-CF_2-O)_9 - \underset{\underset{F}{|}}{\overset{\overset{CF_3}{|}}{C}} - COOH$$
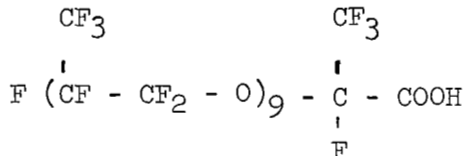
3. HFPO Polymer Acid (M.W. 2600)

$$F(CF-CF_2-O)_{15} - \underset{\underset{F}{|}}{\overset{\overset{CF_3}{|}}{C}} - COOH$$
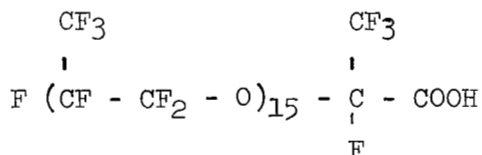
4. HFPO Polymer Acid (M.W. 4200)

$$F(CF-CF_2-O)_{24} - \underset{\underset{F}{|}}{\overset{\overset{CF_3}{|}}{C}} - COOH$$
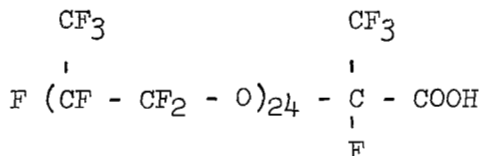
A series of grinding runs with magnetite were initiated in which each of these acids was used as the surfactant. The carrier liquid used

in each case was Freon E-3 fluorinated ether

$$\begin{array}{ccc} CF_3 & & CF_3 \\ | & & | \\ F(CF - CF_2 - O)_3 & - & CH \\ & & | \\ & & F \end{array}$$
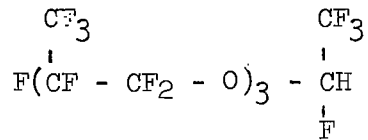
which had optimum viscosity and volatility characteristics.

In all cases, these grinds resulted in the formation of ferrofluids (G118, G119, G146, G151).

The molecular weight of the surfactant did not have a marked effect on the rate of colloid formation, using colloid formation, using colloid density or M_H, fluid magnetization at 10^4 oe, as an index ($K_1 = 3 \times 10^{-3}$ hrs^{-1}). However, a marked effect on the ratio M_L/M_H ($M_L =$ fluid magnetization at $H_L = 116$ oe) was noted. This ratio increased with increasing molecular weight of the surfactant used, from 0.23 for the 1000 molecular weight acid to 0.35 for the 4200 molecular weight acid. As discussed in a later section on fluid magnetization, this finding indicates that the average size of the particles increases with increasing molecular weight of the stabilizing agent used. This was confirmed by electron micrographs of samples of the fluids (see Table 5).

In trying to determine the compatibility of these ferrofluids with different fluorocarbon liquids, it was found that there was an effect of the stability of the colloid in solvents of different molecular weights. These results are summarized in Table 3. A (+) indicates that when a drop of ferrofluid was added to an excess of liquid, the ferrofluid dispersed readily. A (-) indicates that spontaneous flocculation and separation of the solid phase occurs. The transition from a stable to unstable system occurs when the molecular weight of the solvent exceeds the molecular weight of the surfactant by more than 50% for the lower molecular weight surfactants. The ratio of Freon E-3 carrier liquid in the initial drop is negligibly small in comparison to the volume of the liquid to which the drop is added, in the experiments.

It was also observed that a flocculated ferrofluid in a high molecular weight carrier liquid would spontaneously re-disperse with the addition of either a low molecular weight carrier liquid such as Freon E-3, or by the addition of a higher molecular weight surfactant to the system. As an example, a HFPO hexamer acid stabilized ferrofluid flocculates in Krytox AZ. Addition of either Freon E-3 liquid or of HFPO 4200 acid results in spontaneous repeptization of the flocculated colloid.

As a tentative explanation for these results, it is proposed that the stabilizing shell around the individual particles in suspension consists of a mixture of adsorbed surfactant molecules and solvent molecules as

Table 3 - STABILITY OF FLUOROCARBON BASE FLUIDS IN FLUIDS IN FLUOROCARBON LIQUIDS OF

INCREASING MOLECULAR WEIGHT AS A FUNCTION OF SURFACTANT

Carrier Liquid Molecular Weight	Freon E-3 620	Freon E-5 950	Freon E-9 1500	Krytox AZ 1900	Krytox AA 2500	Krytox AB 3600	Krytox AC 5000
Molecular Weight of Surfactant							
1000	+	+	-	-	-	-	-
1660	+	+	+	+	-	-	-
2600	+	+	+	+	+	+	+
4200	+	+	+	+	+	+	+

+ dispersion
- flocculation

shown in Figure 5a. When the solvent molecules are much longer than the surfactant molecules, one end of the solvent molecule extends beyond the adsorbed surfactant molecule as shown in Figure 5b. When this occurs, it is then possible for a given solvent molecule to interact with the ad-sorbed layers of two adjacent particles as shown in Figure 5c. Flocculation ensues as a result of this association. Increasing the ratio of surfactant molecular weight/carrier molecular weight results in repeptization because this increases the physical separation of particles relative to the length of a solvent molecule.

Fluorocarbon base ferrofluids are immiscible with oil water base fluids in general. They retain the immiscibility characteristics of the parent fluid. With water there is some tendency to emulsify which decreases with increasing molecular weight of the surfactant and solvent used. They are miscible with other perfluorinated liquids such as perfluorotributyl amine. They are incompatible with solvents that are soluble or partially soluble in Freon E-3 but differ markedly in chemical structure. These chemicals include perchlorinated solvents such as carbon tetrachloride, or partially fluorinated liquids such as Freon 113 (DuPont) or Fluorolube S (Hooker Chemical Co.).

Ester Base Fluids

For many applications where the ferrofluid will be exposed to the atmosphere, the carrier base has to be non-volatile, very stable and of low viscosity. Prior to the program, all the ferrofluids available were prepared in bases considered too volatile. This included kerosene and even mineral oil base systems. Ferrofluids prepared in Union Carbide Silicone L43 were satisfactory as far as volatility but were too viscous for consideration.

Two very different types of non-volatile ferrofluids were developed during the course of the program. Some of the higher molecular weight fluorocarbon ether base fluids (Krytox AC) with high molecular weight surfactants (HFPO 4200) exhibit this characteristic. Low volatility properties were also obtained with dinonyl phthalate base fluids. These fluids use a much less expensive raw material and are just as suitable for many applications.

Dinonyl phthalate was considered an ideal carrier for many applications because of its stability, reasonable viscosity, and extremely low volatility. Its vapor pressure at $25^{\circ}C$ is less than 10^{-7} torr. This compound is normally used as a vacuum pump oil.

Dinonyl phthalate is too viscous to consider ferrofluid formation in this base by grinding magnetite in its presence. It was decided to form a

Fig. 5a

LOW MOLECULAR WEIGHT
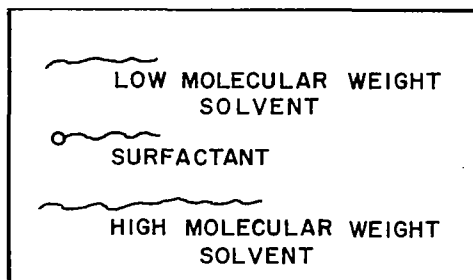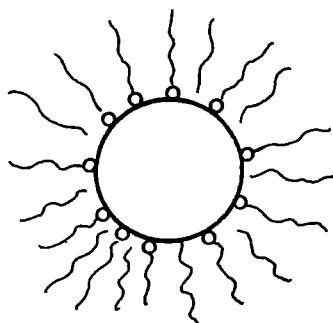SOLVENT

SURFACTANT

HIGH MOLECULAR WEIGHT
SOLVENT

Fig. 5b
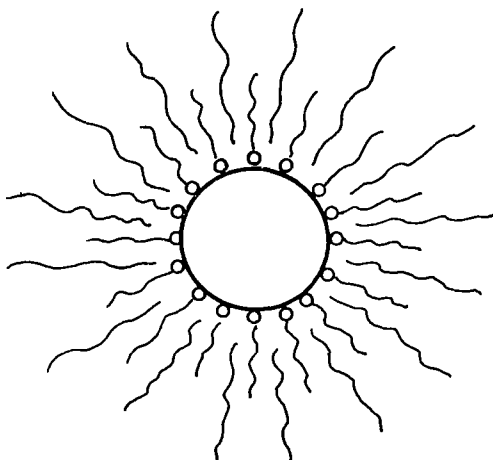
Fig. 5c
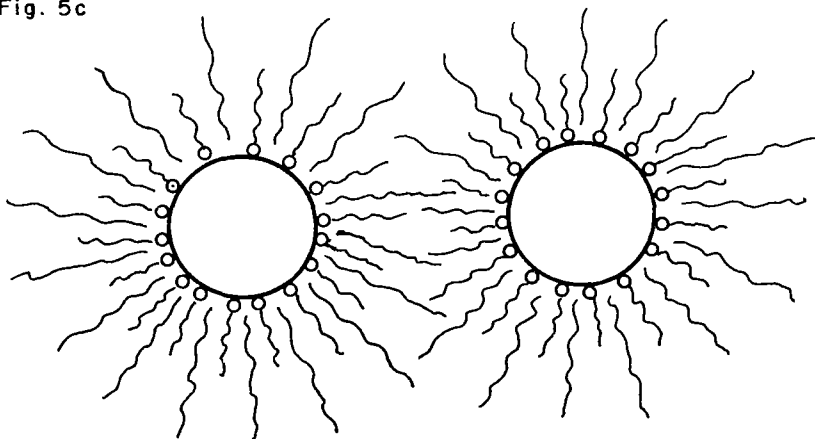
79-0953

Figure 5 EFFECT OF SOLVENT MOLECULAR WEIGHT ON INTERACTION OF PARTICLES

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dinonyl phthalate base ferrofluid by adding it to a hydrocarbon ferrofluid (such as kerosene) and then evaporating the more volatile hydrocarbon leaving as a residue, hopefully, a dinonyl phthalate base ferrofluid.

Addition of dinonyl phthalate to ferrofluids stabilized by such surfactants as oleic acid, Tenlo 70, and Triton X55 which are all low HLB surfactants, resulted in flocculation of the ferrofluid. There was phase separation. However, it was observed that dinonyl phthalate could be safely added to a kerosene base ferrofluid prepared with a less hydrophobic surfactant such as Triton X45 (Rohm and Hass) which is an ethylene oxide adduct of iso-octyl phenol in which the mole ratio is 5 to 1. The kerosene was then removed to yield a dinonyl phthalate base ferrofluid.

The reason why this solvent transfer operation succeeded is in the nature of the surfactant. The surfactant was not so hydrophilic in character that it would be incompatible in kerosene which is a very nonpolar system, but less lipophilic than the other surfactants used in order to be compatible with dinonyl phthalate which is an ester of intermediate polarity. According to the manufacturer, the HLB number for Triton X45 is 10.4 which is essentially near the middle of the range between extremely hydrophilic systems (18-20) and extremely lipophilic systems (2-4).

Preparation of Ferrofluids with Materials of Higher Saturation Magnetization

In Phase I of the program, three separate attempts to prepare ferrofluids by grinding 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 made 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.

The difficulties encountered in the previous grinding runs were believed due to:

    i.   The fact that the powder was easily deformable and would, therefore, not break into smaller fragments during the grinding process.

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

    iii.   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:

i. 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.

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 these materials.

c) Hardened grades of carbonyl iron powders. In addition to the type L iron powder, General Aniline and Film manufactures other powders which are harder. Type SF is similar to type L except that it contains 0.8% carbon which makes it more brittle. Type W in addition, contains 6% N which should further increase the brittleness of these powders. The particle size of these powders is almost 2-4 microns.

d) "Lodex-Round" powders (General Electric Co.). This material consists of finely divided cobalt coated cobalt-iron particles made by an electro-precipitation technique. The particle size is about 500 Å. It was considered the metal most likely to yield a stable ferrofluid.

ii. To eliminate impurities such as water and oxygen, all operations are carried out with dry reagents and under conditions of minimum oxygen contamination.

iii. 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
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 Santolube 393 oil additive).

In addition to the above, a grinding mill was also equipped with
tungsten carbide grinding balls. These balls are much harder, more
abrasion resistant 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.

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 character-
istics of the metal and metal oxide would be similar. These dispersion
tests were run with Carbonyl Iron Powder W (General Aniline and Film Co.),
Carbonyl Iron Powder SF (General Aniline and Film Co.) and with Lodex
round Cobalt-Iron (General Electric Co.); in kerosene in the presence of
different surfactants, as shown in Table 4. Some of the surfactants
tried had a definite effect on the settling rate of the iron powder used,
the Iron SF powder being more affected than 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 magnetite dis-
persants 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 surfactant.

Three grinding runs were started with the 35% cobalt-iron powder (G81, G83, G84). In G81, Santopoid 23-RI, a gear oil additive, was used without any colloid formation whatsoever. In G83 and G84, oleic acid was used as the additive. A difference between the two runs was that tungsten carbide balls were used in G84 while standard steel balls were used in G83. A dark colored supernatant was formed in both cases, but with little colloid formation. After 1640 hours of grinding a colloid with a magnetization of less than 10 gauss was formed in G83 and of negligible magnetization in G84.

A run (G100) was tried with carbonyl iron powder W and Santolube 393 an extreme pressure lubricant additive, without success. Similar poor results were obtained when attempting to grind Lodex Round particles in the presence of ENJAY 3854 polymeric surfactant. Unsuccessful results were also obtained with carbonyl iron powder SF and Triton X45 surfactant.

Table 4 - DISPERSION TESTS OF METAL POWDERS IN KEROSENE

	Settling Time Minutes		
Surfactant	Carbonyl Iron W	Carbonyl Iron SF	Lodex Round
Triton X100	21	over 600	No suspension
Triton X45	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 X35	12		
Triton X15	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)	6		
Enjay 3854 (Humble Oil Co.)	6		
Enjay 3029 (Humble Oil Co.)	6		
Blank	6	7	No suspension

The above runs all were less than 2000 hours in length. One metal grind was allowed to run for a much longer period of time. Silicon-iron powder was ground for over 4000 hours with oleic acid as the surfactant. As with the other runs, very discouraging results were obtained in the first 2000 hours of test. A significant increase in ferrofluid density and saturation magnetization was observed only after 2300 hours of grinding time. Further increases in density and magnetization with further grinding time, up to 4200 hours, have since been observed. The volume fraction solids based on magnetization and density of samples that were spun in a laboratory centrifuge for 10 minutes and 1 hour, respectively are presented in Figures 6 and 7. Assuming a nominal acceleration of 2000 g, 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_d = 15000 gauss ρ_c = 7.2 gr/cm^3) the density 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 30% has been reduced to below 840 Å.

The density measurements yield higher values than the magnetization measurements. This ratio is higher for the product centrifuged 60 minutes than for the product centrifuged 10 minutes. There was also a noticeable drop in magnetization in the product centrifuged for 10 minutes at the end of the grind. This believed due to partial oxidation of the particles in suspension. The smaller particles which have a higher exposed specific surface area would be expected to be more sensitive to such a mechanism. The run was stopped at 4200 hours because of this drop in magnetization in the hope of salvaging a product that could be used as a ferrofluid.

The grind product was partly centrifuged at 4000 g for 10 minutes and at 17000 g for 10 minutes in the usual manner.

Immediately after centrifugation, the first product had a saturation of only about 14 gauss and the other material of less than 5 gauss. The product centrifuged at 17000 g had a volume fraction solids, based on density measurements, of 0.69% which should correspond to a product with a magnetization of slightly over 100 gauss. Upon standing with time, both products became totally unresponsive to magnetic fields.

The slow rate of grind of the metal products is believed to be due to the fact that these metals, while considered brittle, are still much more ductile than magnetite and, therefore, there is less tendency for a crack to propagate. The larger particle size of silicon iron powders presented in the figures also comes into play. The loss of magnetization with time is due to the slow oxidation of the metals in the solvent, either by reaction with the surfactant, oleic acid, or with water. It should be noted that the solubility of water in hydrocarbons containing
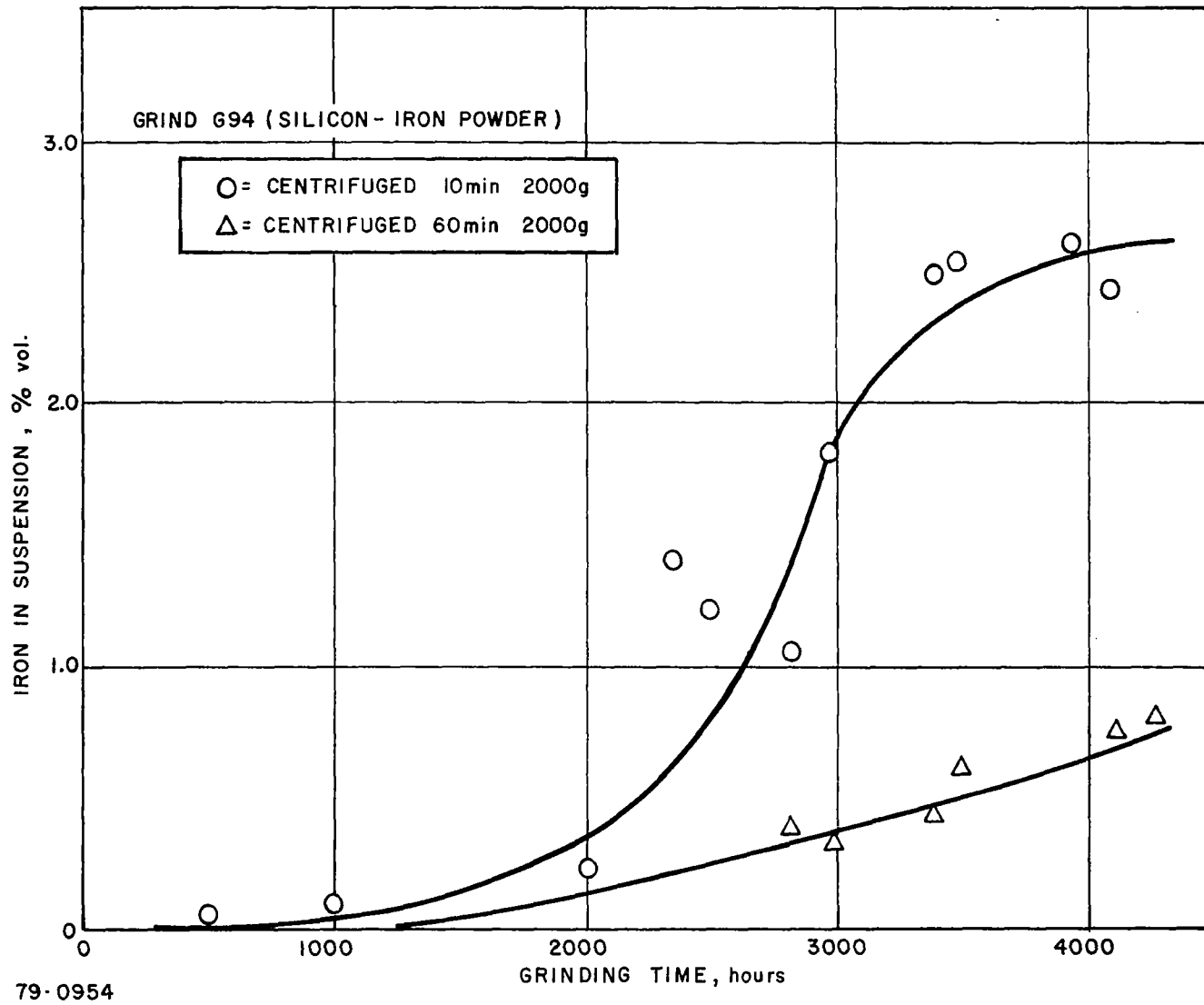
Figure 6 COLLOID FORMATION IN A METAL GRIND BASED ON SOL DENSITY

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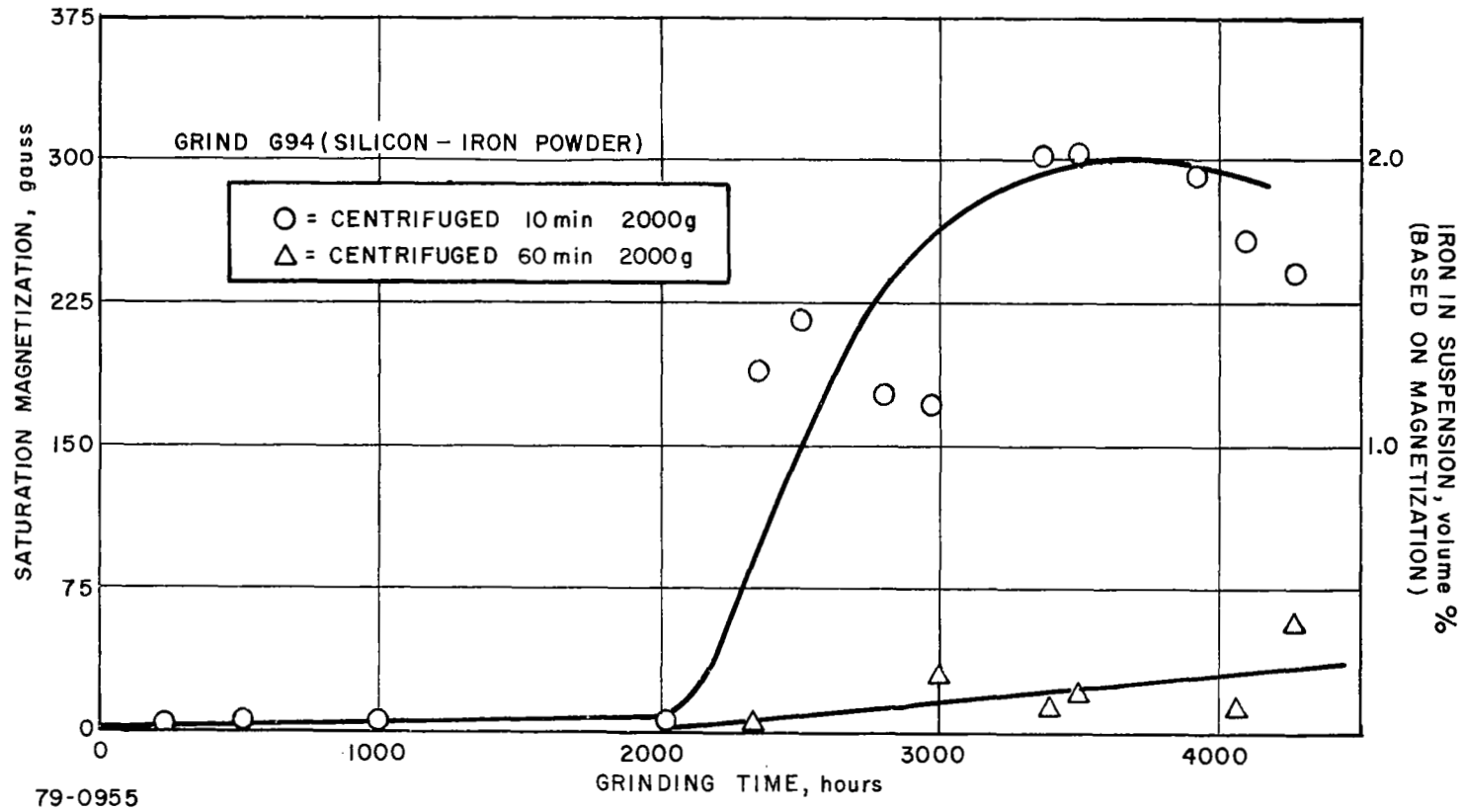
Figure 7 COLLOID FORMATION IN A METAL GRIND BASED ON MAGNETIZATION

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large surfactant concentrations is much higher than in pure hydrocarbon because of micelle formation. Water droplets can be stabilized much in the manner that the magnetic particles are stabilized. These combined results discourage further investigation in the area of the preparation of metal sols by grinding. Alternate possibilities might be electro-deposition of metal particles in mercury, followed by transfer into an anhydrous non-reactive solvent, e.g., suggested by some Russian authors(ref.12).

Further Search for New Surfactants for Magnetite/Kerosene Systems

There was a continuing effort in trying to make magnetite/kerosene ferrofluids with new surfactants. One of the goals was to obtain a better understanding of the effect of surfactant properties such as structure and reactive polar groups on the formation of a ferrofluid. A second goal was to obtain ferrofluids with improved physical properties, such as higher magnetization, greater stability, etc. In these experiments, the principal types of surfactants investigated were carboxylic acids, amines, alcohols and modified polymers.

Carboxylic Acids. - As already reported, the original ferrofluids were magnetite suspensions in kerosene stabilized by oleic acid:

$$CH_3 - (CH_2)_7 CH = CH(CH_2)_7 COOH$$
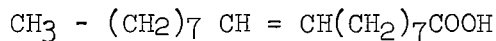
It was found that short chain carboxylic acids with less than twelve carbon atoms did not result in a stable suspension. It was further found that stearic acid, the saturated homologue of oleic acid did not form a stable suspension but that linoleic acid, the doubly unsaturated homologue did result in a ferrofluid.

Further grinds were made with eighteen carbon fatty acids of differing degrees on unsaturation.

The previous results obtained with linoleic acid was confirmed (G120). It was further noted that the rate of colloid formation with this surfactant is the same as with oleic acid.(ref. 13). Ferrofluid formation was also obtained when a commercial linseed oil fatty mixture (Wochem 441)* was used as a surfactant, but at a rate that was 20% slower (G63).

This mixture contained as the principal component, linoleic acid $CH_3(CH_2 - CH = CH)_3(CH_2)_7COOH$, an unconjugated triply unsaturated fatty acid as well as significant quantities of oleic acid and linoleic acid, and some saturated acids.

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* Product of Woburn Chemical Company

A ferrofluid was not formed when a commercial chinawood fatty acid mixture (Wochem 400*) was used (G61). A gel was formed which when broken did not form a magnetically responsive colloid. Wochem 400 is essentially eleostearic acid, $CH_3(CH_2)_3(CH =CH)_3(CH_2)_7COOH$, with minor quantities of the other fatty acids mentioned above. Eleostearic acid differs from linoleic acid only in the position of the double bonds.

A run (G65) was also made with unsaponified linseed oil.* This product is the glyceryl ester of the fatty acid mixture used in grind G63. In the ester, the fatty acid end group is blocked and is not free to react with the magnetite surface. Grinding for over 2000 hours resulted in the formation of a dark viscous liquid but not in the formation of a magnetic colloid.

Other carboxylic acids examined were myristic acid (G68) in kerosene and cinnamic acid (G69) in tetrahydronaphthalene. Neither runs resulted in ferrofluid formation.

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 that increased in thickness with time was observed to form at the surface of the ferrofluids so obtained. It was believed due to the limited solubility of the amines in the hydrocarbons used (ref. 14). 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, the following runs were made:

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

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

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

$$CH_3 - (CH_2)_9 - CH - CH_3$$
$$|$$
$$HN - (CH_2)_3 - NH_2$$
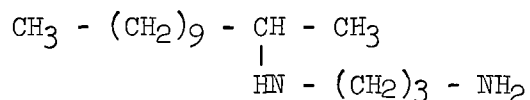
* Product of Woburn Chemical Company

This saturated amine has two reactive groups which could interact with the particle surface, a primary and secondary amine and also is much more soluble in kerosene than aliphatic amines (ref.15) Unfortunately this compound behaved in an analogous manner to the straight chain amines, definite but negligible ferrofluid formation.

4) Oleyl amine (G113): Oleyl amine has the same structure as oleic acid except that the terminal groups differ. The carboxylic group -COOH, is replaced by a primary amino group - CH_2NH_2. This material is also more soluble in kerosene than aliphatic amines. The results of this run were similar to the results of all the previous runs in which amines were used. After 1500 hours of grinding, the magnetization was less than 23 gauss.

Alcohols. - One of the real advances in surfactant chemistry was the realization that ethylene oxide could be used to synthesize surfactants of any degree of lipophilicity or hydrophobicity desired. This comes about because ethylene oxide reacts with any active hydrogen to form an alcohol in the following manner:

$$R - H + CH_2 - CH_2 \quad \xrightarrow{\hspace{2cm}} \quad R - CH_2 - CH_2 - OH$$
$$\diagdown\diagup$$
$$O$$
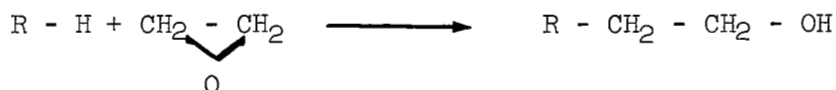
Since the product of this reaction is an alcohol that contains an active hydrogen, it will also react with ethylene oxide

$$R - CH_2 - CH_2 - OH + CH_2 - CH_2 \xrightarrow{\hspace{1cm}} R - CH_2 - CH_2 - O - CH_2 - CH_2 - OH$$
$$\diagdown\diagup$$
$$O$$
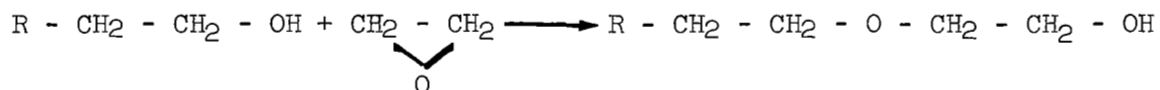
By having a sufficient excess of ethylene oxide any number of ethoxy groups, $-CH_2 - CH2 - O$, can be added to a base molecule. Since the ethoxy group is slightly hydrophilic, as more and more of these adduct links are added to a base molecule, the surfactant becomes more and more hydrophilic. In this manner, it is possible to change a surfactant which has great affinity for non-polar media (aliphatic hydrocarbons) into one which has affinity to polar media such as water.

A series of grinding tests were performed with different ethylene oxide adducts of octyl phenol. These surfactants had the following general formula

$$C_8H_{17} - \bigcirc - (O - CH_2 - CH_2)_n - OH$$
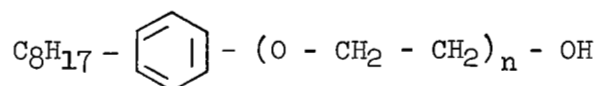
where n is the number of ethylene oxide units added. In this series of tests, the average value of n varied from 1 to 10. Some very interesting results were obtained.

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The shortest chain surfactant, Triton X15 (n = 1) (G111) was not an effective grinding agent. There were only traces of colloid formed even after 1000 hours of grind.

Triton X35 (n = 3) (G105) proved to be the most effective grinding additive of the series for kerosene-magnetite systems. All magnetite was reduced to colloidal dimensions in 1150 hours (see Figure 8). The rate constant is 4×10^{-3} which is comparable to the Tenlo 70 systems. This is not surprising since Tenlo 70 is also a hydroxy terminated ethoxy adduct.

Colloids of ever decreasing stability are obtained as the ethoxy chian length of the molecule is increased. With Triton X45 (n = 5) (G106), a colloidal suspension is formed at about the same rate as with X35. (See Figure 8). However, this colloidal suspension is not stable for long periods of time. It was found to flocculate after a shelf life of about two months.

This lack of stability is even more pronounced with Triton X114 (n = 7-8) (G112). Colloid formation proceeds at the same initial rate as with X35 and X45, but becomes noticeably slower after 400 hours of grind. A peak in the solids concentration is reached at 900 hours and then rapidly decreased. The flocculation process continued after the grind as the solid separated completely while on the shelf.

Increasing the number of ethoxy units to n = 9-10 with Triton X100 (G107), G116) results in absolutely no colloid formation.

Successful colloid formation also resulted when oleyl alcohol was used as a surfactant (G103).

Effect of Surface Structure. - The results of the grinding experiments demonstrate that the structure of the stabilizing agent used is critical. It appears that the principal factors were:

    i.   The nature of the adsorbing group,

    ii.   The rigidity of the adsorbing molecule above a
         certain minimum critical length,

    iii.   The polarity match of the surfactant and the solvent.

It has been found that some surfactants molecules with carboxylic acid end groups and hydroxyl end groups have resulted in ferrofluid formation when added to magnetite being group in kerosene. It has also been that none of the amines used have resulted in any substantive ferrofluid formation. These are unexpected findings since fatty amines normally adsorb quite strongly on polar surfaces such as iron oxides. The amines proved to be
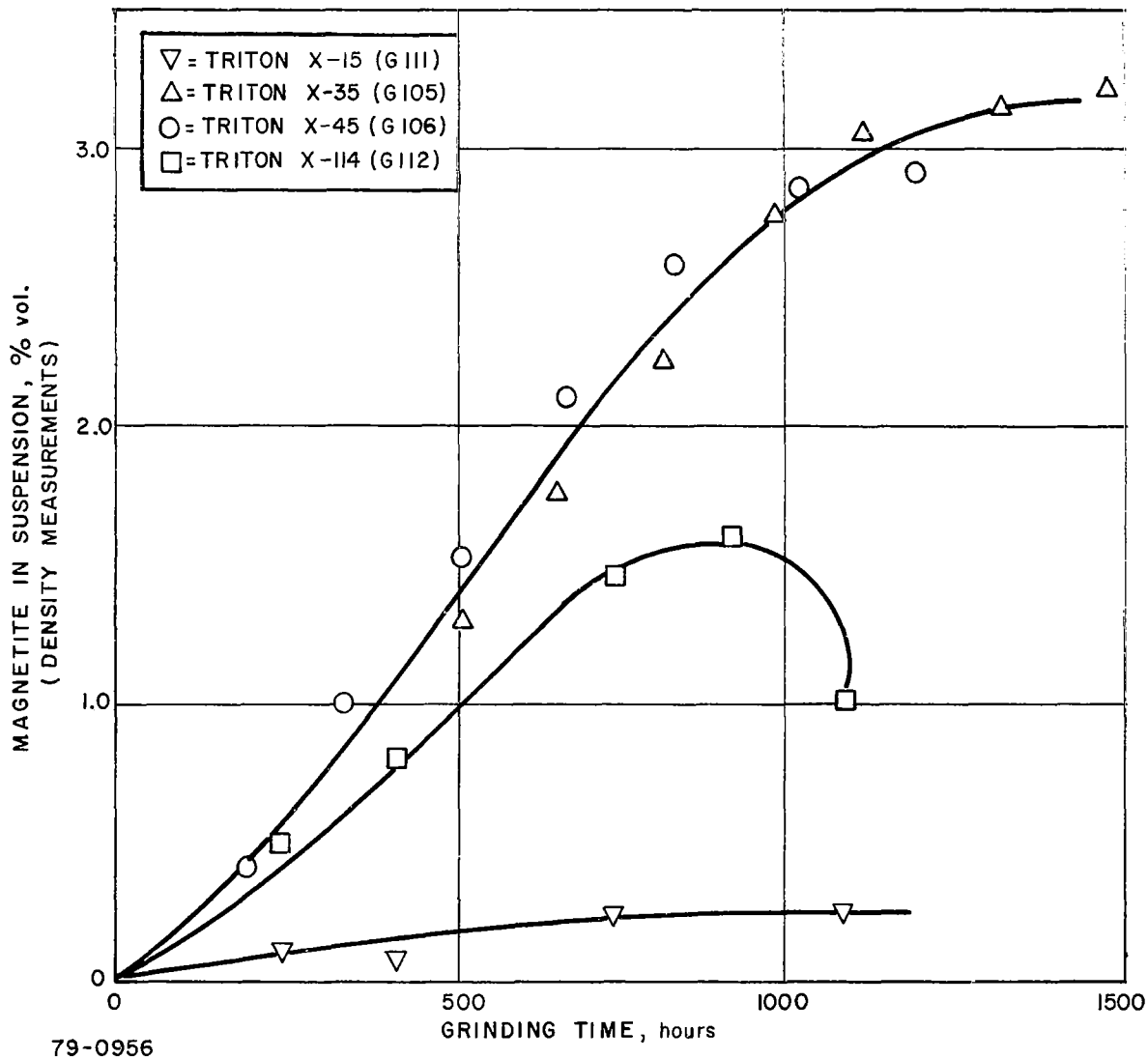
Figure 8 EFFECT OF ETHOXY CHAIN LENGTH OF TRITON SURFACTANTS ON THE
FORMATION OF A FERROFLUID

79-0956

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). The solubility of the amines varied widely from the limited solubility of octadecylamine to the total miscibility of Duomeen L-11. One possible explanation for these results is that grinding of the magnetite occurs because of 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.

The results obtained with the different eighteen carbon fatty acids can be correlated in terms of the solubility of these acids in kerosene. Data have been obtained on the solubilities of linoleic acid, oleic acid, stearic acid and stearolic acid, a triply unsaturated acid (ref. 16) The first two acids exhibit high solubility in hydrocarbons while the latter two exhibit low solubility. Data are not available on the solubility of linolenic acid and eleostearic acid. Based on the results with stearic acid, oleic acid and linoleic acid, the grinding of experiments indicate that the solubility of these compounds in kerosene is limited. The partial ferrofluid formation of grind G63 can be accounted for by the presence of oleic acid and linoleic acid in the product.

The lack of reactivity of myristic acid which is also saturated, is analogous to the behavior of stearic acid.

Molecules below a certain length do not result in particle stabilization. In Phase I, it was found that undecenoic acid which has eleven carbon atoms and one double bond did not result in a ferrofluid, even though it is soluble in kerosene. This molecule on the average is about 12 Å long; oleic acid which forms a stable suspension is about 20 Å long. In this phase of the program, it was found that Triton X15 was not an effective agent as well. Since this molecule is even more lipophile than X35, one explanation is that the surfactant molecule is too short to provide a sufficient stabilizing layer. The principal component of this product is C_8H_{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 X35 has three ethylene oxide units which increases the length of the molecules to about 21 Å. The slight amount of magnetization is because of Triton products which are not pure mono-molecular species, so that Triton X15 contains some longer chained species than the mono-molecular product. Comparison of the results obtained with X15 and X35 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.

The surfactant has to be matched to the solvent. This is evident from the results obtained with the longer members of the Triton X series. The short chain members are soluble in aliphatic hydrocarbons such as

kerosene while the long chain members are not. Triton X15 and X35 are both soluble in kerosene at any concentration level. Triton X45 is much less soluble. It is only soluble at concentrations greater than 10-15%. This is explained by the fact that Triton X45 is a mixture with respect to polyoxyethylene chain length, with five oxyethylene units predominating. The longer polyoxyethylene chain members present are insoluble in refined paraffinic solvents and only at high concentrations of Triton X45 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 X114 and X100 where the average chain lengths increase and the concentration of smaller chain components which act as coupling agents decrease. With X100 in fact, there is no solubility whatsoever.

The decreasing solubility of the surfactant results in decreasing colloid formation and stability. With X35 a stable colloid was formed; with X100 no colloid was formed.

The most interesting results were obtained with the intermediate members where an initially stable colloid was formed that flocculated with time and increasing surface area development. This behavior can be an indication that the shorter molecules in the mixture adsorb preferentially and so form a suspension, but as longer chained more polar surfactants are adsorbed, the compatibility of the particles with the solvent changes and flocculation ensues. If the solvent is changed to a more polar one, then the system should remain stable. This is exactly what was done with the preparation of the ester base ferrofluids.

Polymeric Stabilizers. - All the surfactants listed in the previous sections are monomeric species. Some grinding runs were carried with polymeric dispersants as grinding agents. The materials tested were modified polybutenes marketed by Standard Oil Co. of New Jersey as ENJAY products 3029, 3355, and 3854. In the patent literature, (ref. 17,18) these are described as substituted succinimides made by adding one or more carboxylic group to a high molecular weight polybutene. This complex carboxylic acid can be reacted with a polyamide to form the stabilizing agent. Unfortunately, little more is known about these materials other than that they have been successfully used to stabilize colloidal suspensions of leaded gasoline in lubricating oil at temperatures as high as $600^{\circ}F$. These compounds were included in the program since they offered an alternate potential method of synthesizing a high temperature fluid.

Grinding magnetite with ENJAY 3029 resulted in the formation of a ferrofluid in 1100 hours of grinding with substantial addition of surfactant during the run (95 gr). Grinding with ENJAY 3355 (G90) resulted in a ferrofluid in less than 1000 hours. The rate constant for

this run was $K_1 = 2.7 \times 10^{-3}$ hrs^{-1}. However, both these products flocculated in less than a month while on the shelf.

This was not the case, however, with ENJAY 3854. The product formed with this agent was stable after grinding. In fact, as is discussed in a subsequent section on thermal stability, the ferrofluids resulting from grinds G96 and G101 are the most stable ferrofluids prepared to date. These runs were also very rapid. A product was obtained in less than 500 hours of grinding time in both cases. The rate constant for these runs was $K_1 = 7.8 \times 10^{-3}$ hrs^{-1}. This is twice the rate observed with Tenlo 70/kerosene and nearly three times the rate observed with oleic acid.

It is unfortunate that detailed information is not available on the structure of these polymers. Key information required would be molecular weight, and number and type of polar groups. It is believed that these molecules stabilize a particle in suspension by coiling and adsorbing on the particle surface. However, if there is a mismatch between the length of the stabilizer molecule and the particle diameter, it is conceivable that simultaneous adsorption of a given molecule on more than one particle could occur, as with the Tamol 731/water systems. The polar groups and their spacing are also critical. Rowland et al, (ref. 19) discuss in more detail the structure of macro-molecules adsorbed at a liquid-solid interface.

MAGNETIC PROPERTIES OF FERROFLUIDS

This section reports the principal results obtained on the magnetic properties of a number of magnetite ferrofluids of varying carrier liquid, particle size and particle concentration.

Experimental Measurements

Magnetization Measurements. - The magnetization of a ferrofluid, M, in an applied magnetic field, H, was obtained by a standard search coil technique. The deflection obtained on a ballistic galvanometer when a capsule containing a cylindrical sample of ferrofluid (1.00 in. long x 0.25 in. diameter) is rapidly removed from a search coil placed in a field H, is directly proportional to the fluid magnetization, M. Calibration is against a standard pure nickel sample of equal shape and volume as the ferrofluid. The applied magnetic field could be varied between 116 oe and 10^4 oe. A more detailed description of the apparatus appeared in the Phase I report (ref. 20). It should be noted that the magnetization values presented in the Phase I report are too high by a constant calibration error. A correction factor of 0.745 should be applied to these values.

Particle Size Distribution. - The particle size distribution of different ferrofluids was obtained by measuring the Martin's diameter (ref. 21) of 250 particles on an electron micrograph. The electron micrograph was at maximum magnification (320,000X and then 400,000X). The resolution was of the order of 10 Å.

The cumulative number concentration was plotted against particle diameter on standard log-probability paper. The best straight line was drawn through the data, i.e., the data was fitted to a log-normal distribution. This plot yielded both $\overline{D}_{NG}$, the geometric number average diameter, and σ_G the geometric standard deviation which are needed to calculate other standard diameter by usual methods (ref. 22). It is then possible to calculate the arithmetic average particle volume, $\overline{V}$, where:

$$\overline{V} = \frac{\pi}{6} \ (\overline{D}_{SA}\overline{D}_{LA}\overline{D}_{NA}) \tag{10}$$

and

$\overline{D}_{SA}$ = arithmetic surface average particle diameter

$\overline{D}_{LA}$ = arithmetic length average particle diameter

$\overline{D}_{NA}$ = arithmetic number average particle diameter

Particle Concentration. - A measure of the volumetric concentration of a colloid is obtained from its density ρ :

$$\epsilon_D = \frac{\rho - \rho_L}{\rho_c - \rho_L} \tag{11}$$

where

ϵ_D = volumetric concentration of solids in suspension based on density

ρ_c = density of solid particle core in suspension

ρ_L = density of the liquid phase

The value of ρ is easily obtained in a tared pycnometer. The value, ρ_c, is the density of the magnetic solid in suspension which is a well-defined parameter. It is presumably independent of particle size. The density of the liquid phase, ρ_L, is the density of the solvent/ stabilizing agent mixture. In many instances, these values are similar and ρ_L can be taken to be the solvent density, ρ_o.

Materials

The ferrofluids that are considered in this section varied widely in composition and properties. They are listed below:

1. **G-4-5-6 Fluid** - This fluid is the product of combined grinds G4-5-6 that was centrifuged in the standard manner. It is a kerosene-oleic acid-magnetite system.

2. **G-44 Fluid** - This fluid is the product of grind G-44 that was centrifuged in the usual manner. It is a kerosene-Tenlo 70 magnetite system.

3. **G-21 Fluid** - This fluid is the product of grind G-21 that was centrifuged in the usual manner. It is a kerosene-oleic acid-magnetite system.

The properties of the above three fluids and products of increasing magnetization obtained from these fluids by vacuum evaporation were reported in the Phase I report (ref. 23).

4. **Fluid 1006** - This fluid was obtained from grind G-64 (heptane - oleic acid - magnetite). 500 ml of G-64 fluid were diluted with 150 ml of kerosene to yield a product with a magnetization of 52 gauss at 10^4 oe. This intermediate was centrifuged at 17000 g for 2 hours. The upper two-thirds of the liquid from the centrifuge tube was then concentrated under vacuum to yield the product.

5. **Fluid 1008** - This fluid was obtained by a) diluting 400 ml of centrifuged product from grind G-77 (kerosene-Tenlo 70-magnetite) with kerosene to 40 gauss at 10^4 oe.; b) centrifuging this intermediate for 1 hour at 17000 g; c) removing the top two-third fraction and d) reconcentrating by vacuum evaporation.

6. **Fluid 1032** - This fluid was obtained from the sediment at the bottom of the centrifuge tubes after grind G-77 was centrifuged for 10 minutes at 17000 g. This sediment was redispersed in kerosene that contained an excess of Tenlo 70. This intermediate was then placed in a magnetic concentration cell for one week. Fluid 1032 is the gap product from this operation, centrifuged for 10 minutes at 2000 g. The amount of kerosene was varied to obtain samples of different magnetization and viscosity.

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7. Fluid 1042 - Fluid 1042 is the product from grind G118
    (Freon E-3-HFPO Decamer acid-magnetite) centrifuged
    in the usual manner. The concentration of samples
    of this liquid was varied to obtain measurements of
    viscosity as a function of magnetization.

8-9. Fluids 1043 and 1044 - A 128 gr sample of Fluid 1042 was
    placed in a magnetic concentration cell. After 216 hours
    the fluid outside the pole faces (bulk fluid) was
    separated from the fluid between the pole faces of the
    magnet (gap fluid). Fluid 1043 is the gap fluid while
    Fluid 1044 is the bulk fluid. The two cuts weighed
    32.9 gr and 95.3 r, respectively.

10. Fluid 1054 - Fluid 1045 is the product from grind G119
    Freon E-3-HFPO Decamer acid-magnetite) centrifuged in
    the usual manner. Different samples of this liquid
    were concentrated to obtain measurements of viscosity
    as a function of magnetization.

11-12. Fluids 1046 and 1047 - Fluid 1046 is the gap liquid and
    Fluid 1047 is the bulk liquid obtained from a 129 gr
    sample of Fluid 1045 after 216 hours in the magnetic
    concentrator. The gap fluid weighed 17.5 gr and the
    bulk fluid weighed 111.1 gr.

13-14. Fluids G80T and G80B - These fluids are the product of
    grind G80 (Water-Tamol 731-magnetite). As mentioned
    already in a previous section, this grind had shown
    some anomalous behavior at the end of the run.
    However, since this was the first water base dispersion
    prepared up to that time, it elicited some curiosity.
    The grind product was centrifuged for 10 minutes at
    17000 g. A large fraction of the solids in suspension
    sedimented. These bottoms were redispersed in
    distilled water and centrifuged for 2000 g. for 10
    minutes. The resulting liquid was called G80B
    (bottoms). The overhead product from the first
    centrifugation was called G80T (tops). G80T was
    stable for about 6 weeks and then turned into a
    gel which was repeptized by addition of more
    stabilizing agents.

15. Fluid 1048 - This is the product from grind G104
    (Water-Aerosol C-61 magnetite). Samples of this
    liquid were concentrated by vacuum evaporation to
    obtain magnetization viscosity curves.

16. Fluid 1068 - This fluid is the product of grind H-1 (Kerosene-Tenlo 70-magnetite), prepared in a 27 gallon mill (Table 2).

17. Fluid 1069 - Samples of Fluid 1068 were subjected to magnetic dialysis in a 2000 oe/cm magnetic field gradient for periods varying from 24-48 hours. About 20% of the original feed liquid remained suspended in the cell in a 2500 oe field. The combined product of numerous experiments was Fluid 1069 (Table 2).

18. Fluid 1070 - Samples of Fluid 1069 were subjected to a second stage of magnetic dialysis as described above. The core liquid of these experiments was Fluid 1070 (Table 2).

Experimental Results

Magnetization curves for three ferrofluids of different average particle size saturation magnetization and carrier liquid are presented in Figure 9. It was found that the average size of the particles in suspension has a major effect on the shape of the magnetization curve.

This is shown by plotting M_L/M_H against average particle diameter $\bar{D}$, as is done in Figure 10 for a number of different fluids. M_L is the fluid magnetization in a low applied field ($H_L = 116$ oe), M_H is fluid magnetization in a high applied field ($H_H = 10^4$ oe). The ratio M_L/M_H is a measure of the shape of the magnetization curve. $\bar{D}$ is an average particle diameter defined as

$$\bar{D} = (\bar{D}_{SA}\bar{D}_{LA}\bar{D}_{NA})^{1/3} = \frac{\pi}{6} \bar{V}^{1/3} \qquad (12)$$

The value of $\bar{D}_{NG}$ and σ_G from which $\bar{D}$ is obtained for each fluid are presented in Table 5.

It was already reported that the high field magnetization, M_H, of a ferrofluid increases linearly as the volumetric fraction solids in suspension increases, $M_H \sim \epsilon_D$. There is little effect of M_H on the shape of the magnetization curve. For some fluids at high values of M_H (~ 700 gauss) there was a slight increase in the ratio M_L/M_H.

If every particle in suspension were an aligned single domain, the ratio of M_H/M_d would be a direct measure of the volumetric concentration of solids in suspension. The ratio of this measure of particle concentra-
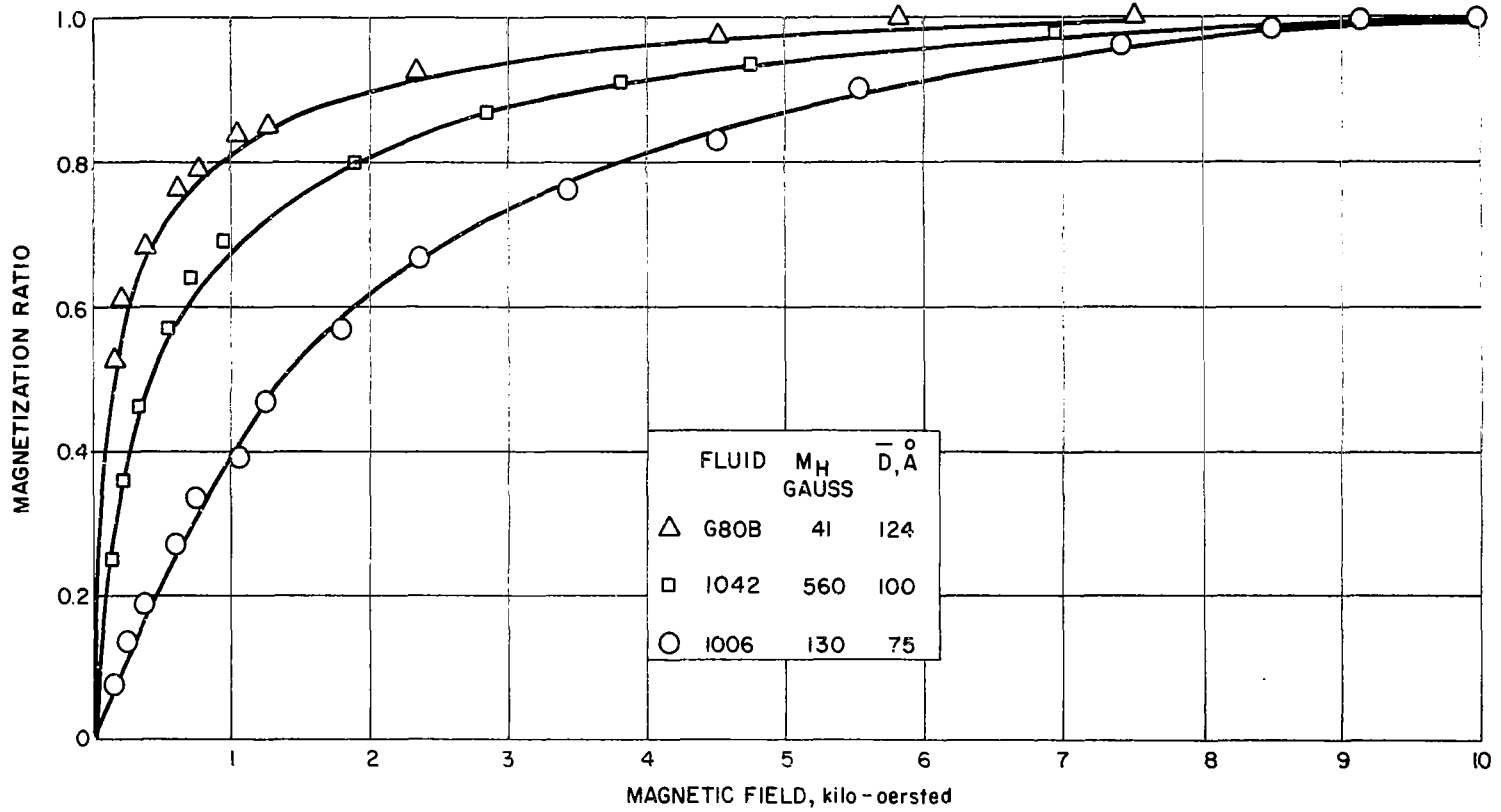
79-0481

Figure 9 MAGNETIZATION CURVES FOR DIFFERENT FERROFLUIDS
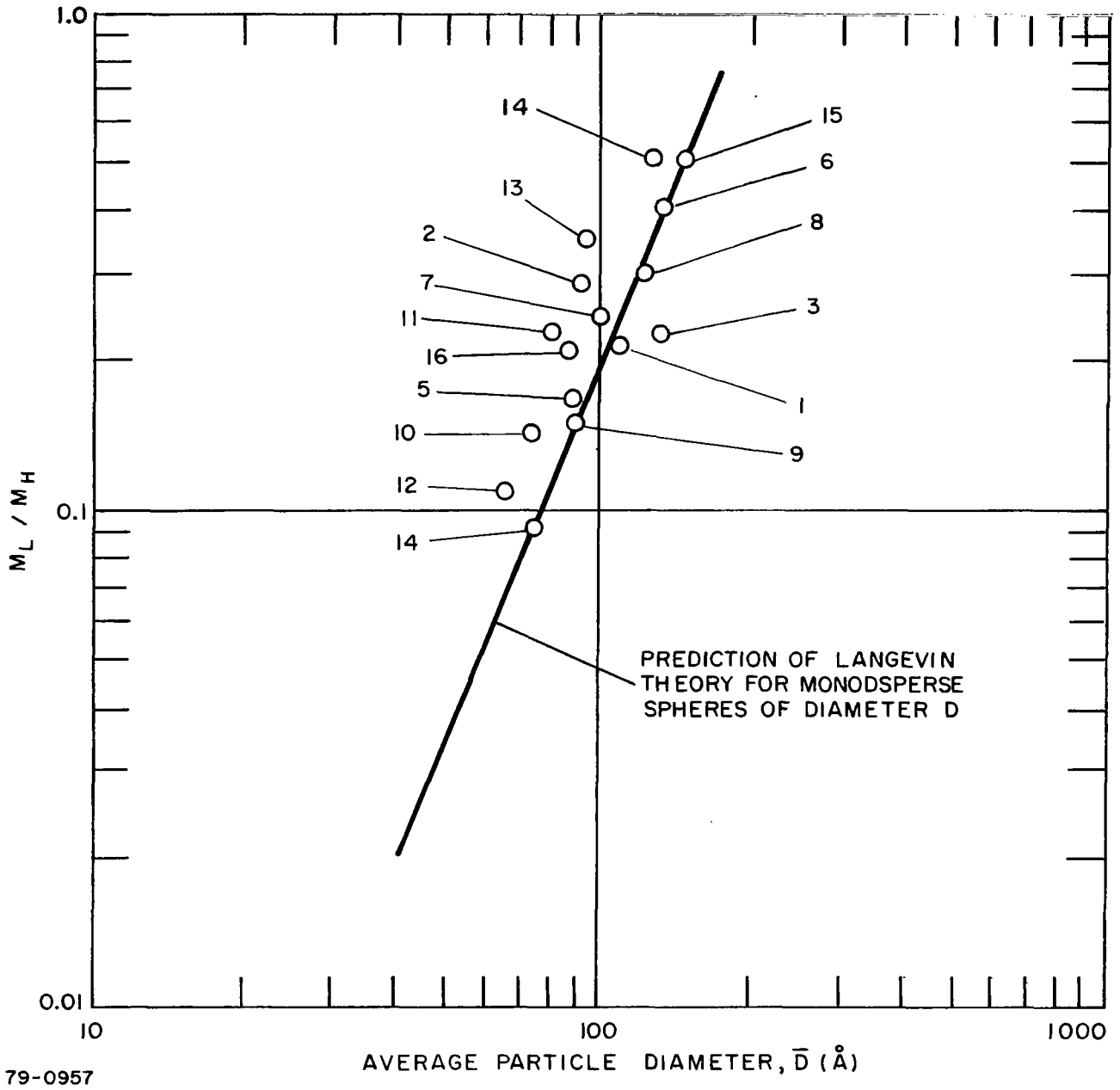
Figure 10 RATIO OF $\dfrac{M_L}{M_H}$ AS A FUNCTION OF AVERAGE PARTICLE

79-0957

Table 5 - SIZE DISTRIBUTION OF COLLOIDAL MAGNETITE IN FERROFLUIDS

Data Point	Fluid	$\overline{D}_{NG}$, Å	σ_G	$\overline{D}$ Å	M_L/M_H
1	G4-5-6	98	1.32	110	.214
2	G44	72	1.46	90	.288
3	G21	115	1.37	134	.212
4	1006	48	1.73	75	.091
5	1008	56	1.73	88	.105
6	1032	86	1.75	136	.42
7	1042	50	1.98	100	.246
8	1043	76	1.73	120	.299
9	1044	45	1.96	88	.150
10	1045	47	1.70	72	.144
11	1046	55	1.64	80	.229
12	1047	40	1.75	64	.109
13	G80T	74	1.48	92	.352
14	G80B	83	1.66	124	.525
15	1048	98	1.63	140	.505
16	1063	52	1.78	86	.22

tion, which is designated as ϵ_M, can be prepared to the volumetric particle concentration obtained by density measurements, ϵ_D.

In all cases, it was found that

$$K = \frac{\epsilon_M}{\epsilon_D} < 1$$

are shown in Table 6. The value K is a measure of non-magnetic solid inclusions that are suspension and was called the conversion factor. It was found that K increases with $\overline{D}$ for different fluids investigated, as shown in Figure 11.

Discussion of Magnetization Results

Theory. - The experimental results can be interpreted by treating a ferrofluid as a suspension of independent, subdomain, superparamagnetic · particles. According to this theory, the magnetization of a ferrofluid is represented by the following equation:

$$\frac{M}{\epsilon M_d} = \frac{\sum_{i=1} \left[\coth\left(\frac{v_i M_d H}{4\pi kT}\right) - \frac{4\pi kT}{v_i M_d H} \right] n_i v_i}{\sum_{i=1} n_i v_i} \tag{13}$$

In the above equation, k is Boltzman's constant and the other terms are defined in the next paragraph.

According to this equation, the magnetization of a fluid M due to a magnetic field H at a given temperature T, is a function of the following parameters:

a. The domain magnetization of the magnetic substance in suspension M_d, e.g., composition of the suspensoid.

b. The particle distribution of the suspensoid, n_i being the concentration of particles of volume v_i.

c. The volumetric concentration of magnetic powder in suspension, ϵ.

The assumptions implicit in the above equation are that

a. The particles are sub-domain in size which establishes a critical upper limit to particle size.

Table 6 - EFFECT OF AVERAGE PARTICLE DIAMETER ON TRANSLATION

OF MAGNETIC PROPERTIES TO A FERROFLUID

Symbol	Fluid	Average Particle Diameter, $\bar{D}$, Å	Fluid Density, ρ, gr/cm^3	Volumetric[a] loading, ϵ_D, percent	Magnetization of Fluid[b] M_H, gauss	Volumetric[c] loading, ϵ_M, percent	Conversion $K = \epsilon_M/\epsilon_D$
1	G4-5-6	110	0.859	1.52	47	0.84	0.55
2	G44	90	0.953	3.99	162	2.90	0.72
2	G44	90	1.500	16.6	685	12.1	0.73
4	1006	75	1.131	7.90	130	2.30	0.29
5	1008	88	1.340	12.8	432	7.65	0.60
6	1032	136	0.902	2.44	102	1.81	0.75
7	1042	100	1.815	2.76	88	1.55	0.56
8	1043	120	1.885	4.89	167	2.95	0.60
9	1044	88	1.795	2.14	62	1.09	0.52
10	1045	72	1.820	2.68	83	1.42	0.53
11	1046	80	1.930	6.10	197	3.48	0.57
12	1047	64	1.810	2.60	68	1.20	0.46
14	G80B	124	1.037	0.95	41	0.73	0.78
15	1048	140	1.1 5	2.40	113	2.01	0.84
16	1068	86	0.917	2.78	104	1.90	0.68

[a]Based on density measurement: $\epsilon_D = \dfrac{\rho - \rho_L}{\rho_c - \rho_L}$

[b]At H = 10,000 oersted

[c]Based on magnetization measurement: $\epsilon_M = \dfrac{M_H}{M_d}$
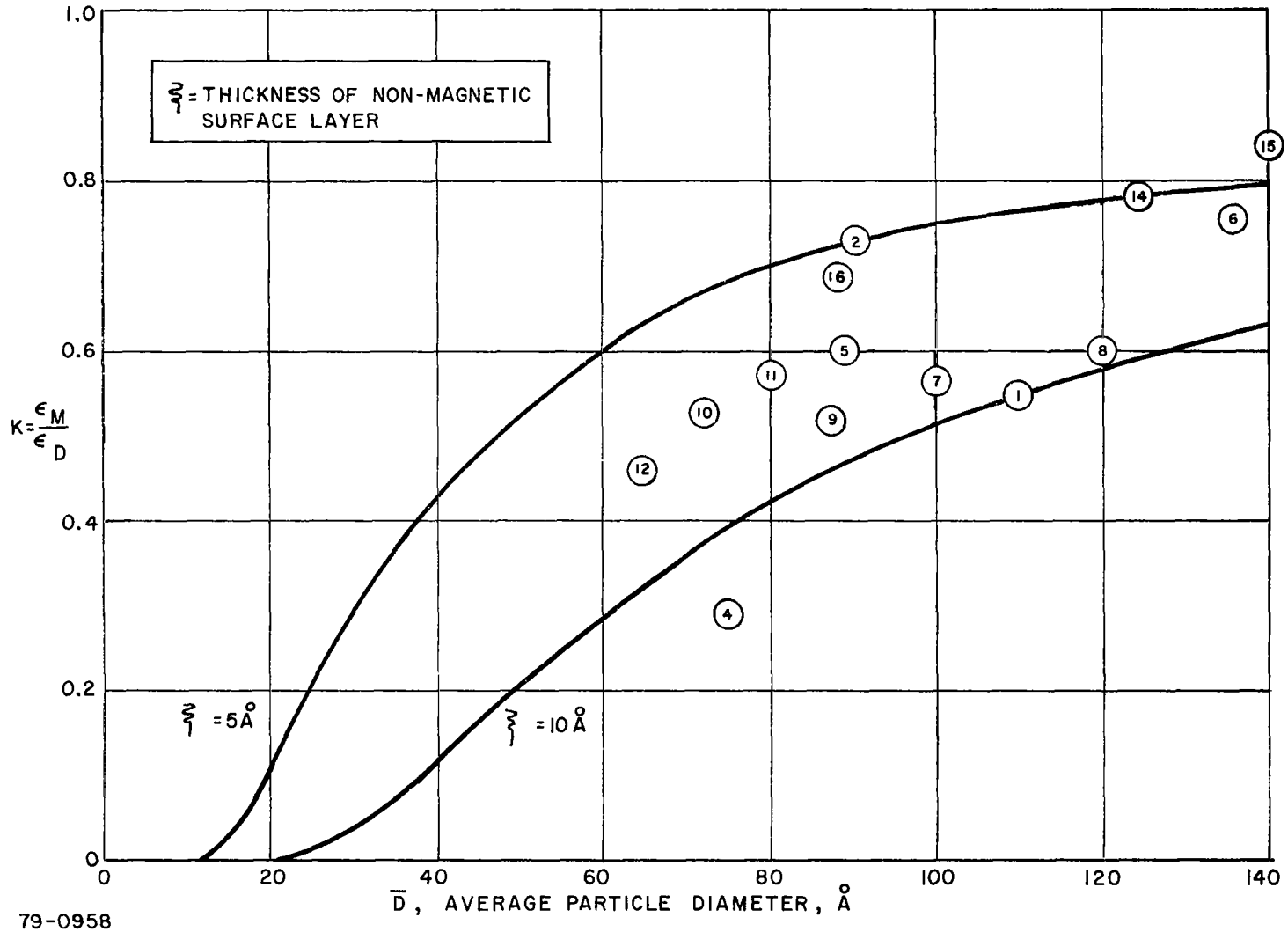
Figure 11 TRANSLATION OF MAGNETIC PROPERTIES OF PARTICLES TO A FERROFLUID

79-0958

b. There is no interaction between the particles. Such interactions would occur if the particles are improperly shielded or possibly too closely packed.

In accordance with this theory, it was found that:

a. the size of the particles in suspension had a major influence on the magnetization characteristics,

b. fluid magnetization increased as the particle concentration,

c. the carrier fluid was magnetically inert.

Effect of Particle Size. - The experimental values of the ratio M_L/M_H as a function of average particle diameter $\overline{D}$ for the different ferrofluids, were compared to the values of M_L/M_H that would be obtained with monodisperse superparamagnetic suspensions of magnetite as a function of particle diameter. The value of $M_L/\epsilon M_d$ and $M_H/\epsilon M_d$ are each unique functions of particle diameter D as shown in Figure 12. As can be seen in this figure, $M_L/\epsilon M_d$ varies rapidly with diameter in the 50 Å - 150 Å range, but that $M_H/\epsilon M_d$ varies little in the same size range and furthermore approaches saturation for particles larger than 80 Å.

Since each curve is a unique function of D, the ratio

$$\frac{\dfrac{M_L}{M_d}}{\dfrac{M_H}{M_d}} = \frac{M_L}{M_H}$$

is also a unique function of D. This ratio is furthermore, independent of particle concentration.

The calculated value of M_L/M_H as a function of D for a monodisperse system of magnetite spheres is also plotted in Figure 10. The experimental parts follow this curve quite closely. This finding supports the assumption of super-paramagnetism.

The correlation is better than expected from the results of electron micrograph counts. There was poor concordance between two separate counts, especially for the smaller sized systems. This was already discussed in Phase I with the counts for grind G44 (ref. 18). The principal reasons are:
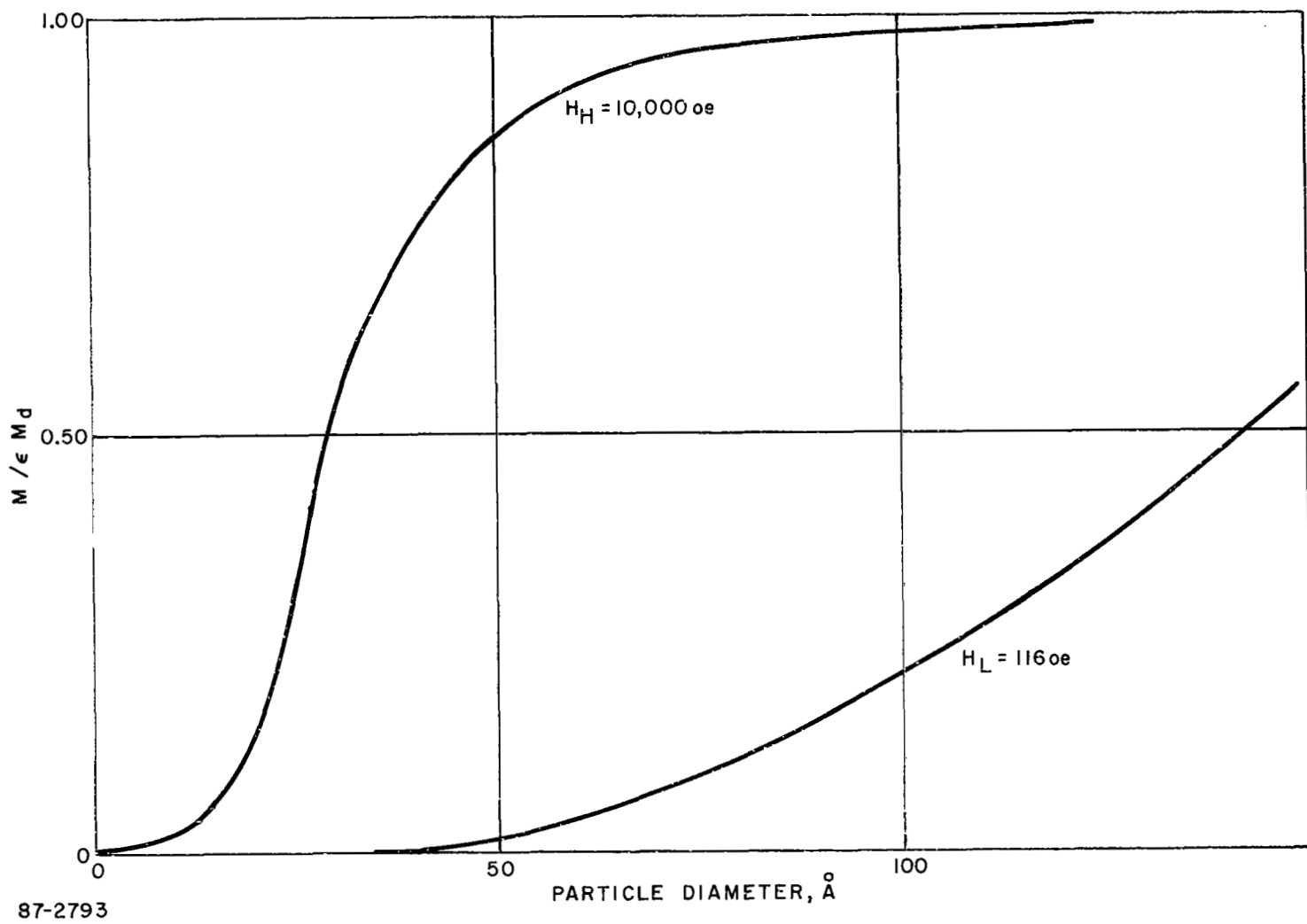
87-2793

Figure 12 MAGNETIZATION OF EQUAL SIZED PARTICLES OF MAGNETITE
(M_d = 5660 GAUSS) IN HIGH AND LOW FIELDS AS A
FUNCTION OF PARTICLE SIZE

i. The particle size is approaching the limit of
    resolution of the instrument which is 10 Å.
    Even at 400,000 X, particles smaller than 30 Å
    in diameter can at best be discerned, but not
    measured.

ii. There is particle agglomeration in some of the
     photographs. It is difficult to discern
     between a mass of small particles and a large
     particle.

If there had been extensive association between particles in the fluid,
the extent of agglomeration would have increased sharply with
increasing particle concentration. The ratio M_L/M_H would have increased
in turn. In general, this was not observed.

Effect of Carrier Liquid. - It is to be noted that these results
include ferrofluids prepared in different carrier liquids. This confirms
the point that the magnetic properties are solely due to the suspended
particles.

Conversion of Particle Magnetic Properties. - It was found that the
volume concentration solids calculated from density measurements was
always higher than would be predicted from the high field magnetization
of the fluid. Three different arguments can be proposed to account for
this feeling:

i. The presence of discrete non-magnetic particles in
    suspension introduced by the grinding operation,

ii. Incomplete saturation of the ferrofluid due to
     super-paramagnetic effects,

iii. Formation of a magnetically inactive surface layer.

The increase of the conversion K with $\overline{D}$ suggests a relationship
involving the surface to volume ratio of the particles. The system
could be treated as though each core particles consists of a magnetic
kernel surrounded by a non-magnetic mantle of thickness, ξ . The
conversion could then be expressed in terms of the ratio $\xi/\overline{D}$ as follows

$$K = (1 - 2 \ \xi/\overline{D})^3 \qquad\qquad (14)$$

The solid lines drawn in Figure 11 are generated by assuming values
of $\xi = 5$ Å and $\xi = 10$ Å. The data fall essentially in the region
enclosed by these lines. One can speculate as to the cause of such a
non-magnetic mantle, which could be of either mechanical or chemical origin.

A non-magnetic layer could be due to the grinding action of the mill. One possibility is that "micro-cracks" are formed on breakage and that these micro-cracks alter the crystal structure of the particles. The particle is, therefore, partially demagnetized. Richter and Dietrich(ref.25) found that the specific saturation magnetization of barium and strontium ferrite decreases with increasing milling time but this reduction disappears if the powders are annealed at about 1000°C. They argued that milling introduces lattice defects into the particle structure. Attempts were made to determine the effects of annealing on the magnetization of particles from a ferrofluid that had been evaporated to dryness. This powder still contained an extensive organic coating which had to be removed. Heating of the coated particles in air resulted in removal of the organic coating and also in a substantial reduction in magnetization of the powder presumably due to partial oxidation of the magnetite. Removal of the organic coating under non-oxidative conditions would not be any more satisfactory because of the possibility of reducing magnetite to FeO or Fe. Another possiblity is that during the grinding operation, the particles abrade the all and that the abrasion products adhere to the surface of the magnetic particles by secondary valence forces. It is not possible to distinguish between magnetic and such non-magnetic particles on the electron micrographs.

A non-magnetic surface layer could be due to chemical action as well. The surface atoms of magnetite could react with an adsorbed species, such as an oleic acid, to form a non-magnetic iron carboxylate. The surface atoms could also be oxidized to non-magnetic Fe_2O_3.

A dried sample of ferrofluid 1042 was examined by x-ray diffraction for the presence of a non-spinel phase. Line broadening due to the small size of the particles interfered with the measurements. Only a spinel phase was detected. This technique also gives an alternate measure of the average particle volume. A volume of $\overline{D}$ of 90 Å + 10 Å was found for this ferrofluid which is in good agreement with the other measurements.

Other possible reasons for the lack of complete conversion of magnetic properties are formation of discrete non-magnetic particles and super-paramagnetic effects.

While a certain amount of contamination is expected from wear of the balls in the grinding operation, much wider variations in K would have been expected for the different fluids studied because of the variation in post-grinding treatment. For example, fluids 1006 and 1008 were subjected to extensive centrifugation, fluid 1042 was only subjected to standard centrifugation while fluids 1043 and 1044 are the bulk and gap fluids obtained from magnetic dialysis of 1042. If the system consisted of discrete magnetic and non-magnetic particles, a marked increase in magnetization should have been observed in a gap fluid and a marked decrease in the bulk fluid. This was never observed even after repeated cycling of a ferrofluid through the magnetic dialyzer.

It will be recalled that M_H is based on magnetization measurements in a 10^4 oe field so that some of the smaller particles in suspension might not be saturated and thus the total magnetite content is not detected. This effect would become more important with decreasing particle size. With limited magnetic fields, the magnetization saturation of a fluid can be obtained from a plot of fluid magnetization, M versus 1/H and extrapolating to the ordinate. For fluid 1006 this technique yields a value of M_H = 200 gauss as compared to a value of M_H = 175 gauss (H = 10,000 oe). For this most finely divided system, super-paramagnetic effects only account for 12 percent of the magnetization loss.

Inherent in the above discussion is the assumption that the domain magnetization, M_d, is a material constant and is size independent. Langevin theory was applied in the present treatment to a system of magnetic particles that are subjected to thermal motion and are freely suspended in a liquid medium. Magnetization of the liquid in a magnetic field is due to the alignment of the magnetic vector of the individual particles by rotation of the particle as a whole. Possible super-para-magnetic effects within a particle and rotation of the magnetic vector within a particle were not considered. If there is a combined Langevin effect due to disorder among a family of particles, then the present treatment of the magnetization properties is invalid. A simple method of testing this hypothesis is to measure the magnetization curve of a sample of a ferrofluid at two temperatures. The first measurement is performed above the freezing point of the corner liquid and the second at a temperature below the freezing point. If there is a combined Langevin effect, after correcting for temperature, a difference in the magnetization curves should be observed.

VISCOSITY OF FERROFLUIDS

Introduction

The viscosity studies initiated in the first phase of the program were continued. The principal areas investigated were:

1) Measurement of the viscosity of a number of ferrofluids as a function of magnetization and shear rate,

2) Determination of the effect of the surfactant on the viscosity of a ferrofluid,

3) Development of fluids of lower viscosity and higher magnetization,

4) Measurement of the effect of an applied field on the viscosity of a magnetic fluid.

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Experimental Method

The viscosity of ferrofluids was measured in a Wells-Brookfield cone/plate microviscometer rather than in the capillary tube viscometers used in the previous phase of the program. In this device the fluid is placed between a flat plate and a rotating cone and the viscosity is obtained from the torque necessary to keep the cone in rotation at a given speed. The cone/plate viscometer is well suited to the needs of the present program:

i.   A very small sample (1.0 cc) is required for the measurement.

ii. It is possible to measure viscosity over a range of discrete shear rates. The instrument was designed to measure viscosities in the range 0-2000 cp at discrete shear rates which varied incrementally from 1.15 sec^{-1} to 230 sec^{-1}.

iii. In addition to standard measurements at constant rate of shear it is possible to measure the viscosity of more viscous liquids at lower variable rates of shear by a torque relaxation technique (ref. 26) technique extended the normal range of the instrument by two orders of magnitude.

iv. With some modifications it is possible to measure viscosity in a magnetic field. With this instrument the small sample size means that a correspondingly small uniform field volume has to be generated. There is no overall bulk motion of the fluid which could be accelerated by gradients and thus result in erroneous values. Furthermore, the complete assembly exposes essentially no free fluid surface so that the problem of surface instabilities (spikes) formed a ferrofluid in the presence of normal magnetic field is minimized. The modifications essentially entail the separation by a flexible shaft of the motor and gears, which are susceptible to magnetic fields, from the cone/plate assembly and sensing head which are made of non-magnetic materials. The cooperation of Brookfield Engineering Laboratories in the necessary modifications is gratefully acknowledged.

Viscosity Measurements of Typical Ferrofluids

The variation of viscosity with magnetization, M_H, was measured over a decade of shear rates for a number of ferrofluids in the absence of a magnetic field. Typical results are presented in Figure 13 for a water base fluid (1048), a fluorocarbon base fluid (1045), and two kerosene base systems, fluid G44 one of the strongest fluids prepared during the first phase of the program, and fluid 1032, a fluid of lower viscosity produced during the present program. In all cases, there is an increase in viscosity with magnetization that becomes more pronounced with increasing magnetization until a limiting magnetization value is reached. All the liquids exhibit Newtonian behavior in regions of low magnetization but develop non-Newtonian flow characteristics that are more or less pronounced depending on the system, as the limiting magnetization is reached. This is demonstrated for one fluid (1048) in Figure 14.

In addition to the evident effects of solvent viscosity and magnetization, the viscosity of a ferrofluid depends on other parameters which are not explicit in Figure 13. The principal factor which still has to be taken into account is the presence of a stabilizing layer around the particles which increases the apparent volume fraction occupied by the solid particles in suspension -- call this volume fraction, ϕ.

It was shown by Einstein that the viscosity of a dilute suspension of rigid non-intersecting spheres, η_s, is higher than the viscosity of the pure liquid, η_o, because of an increased dissipation of energy produced by modification of the fluid motion near the particle surface. This relationship can be expressed as follows

$$\frac{\eta_s}{\eta_o} = 1 + 2.5 \, \phi \tag{15}$$

Equation 15 is valid only for small values of ϕ where the flow disturbance created by one particle does not affect the rest of the system. At higher values of ϕ this assumption is not valid and the overall viscosity is no longer the same individual effects. Numerous empirical equations have been developed to treat the viscosity of concentrated suspensions. These have been reviewed recently by Sherman (ref. 21). In the present work, a procedure introduced by DeBruyn was used to characterize the viscosity of ferrofluids. This relationship is of the form

$$\frac{\eta_s}{\eta_o} = \frac{1}{1 - 2.5 \, \phi + f \, (\phi_c) \, \phi^2} \tag{16}$$
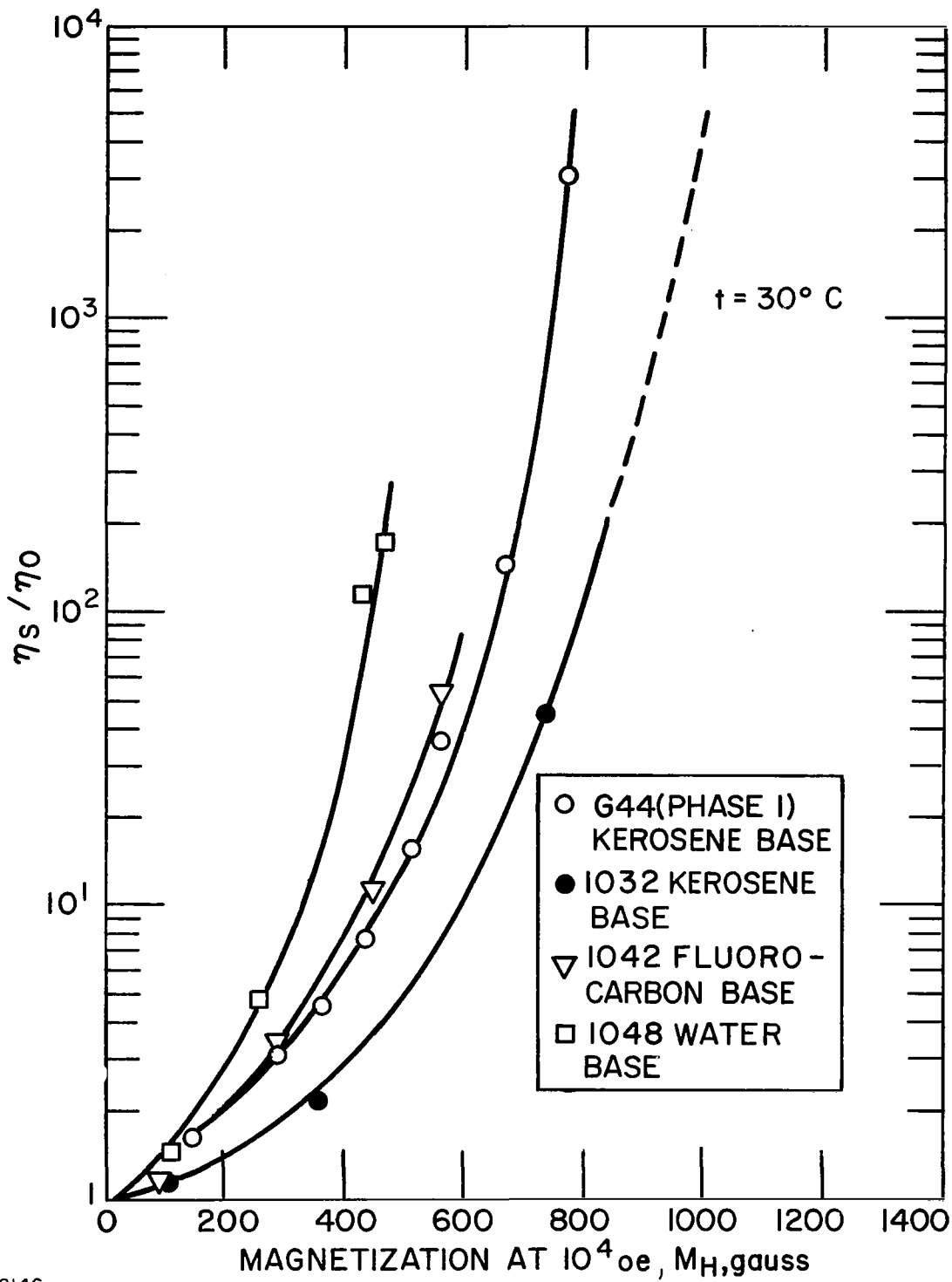
Figure 13 FLUID VISCOSITY AS A FUNCTION OF MAGNETIZATION

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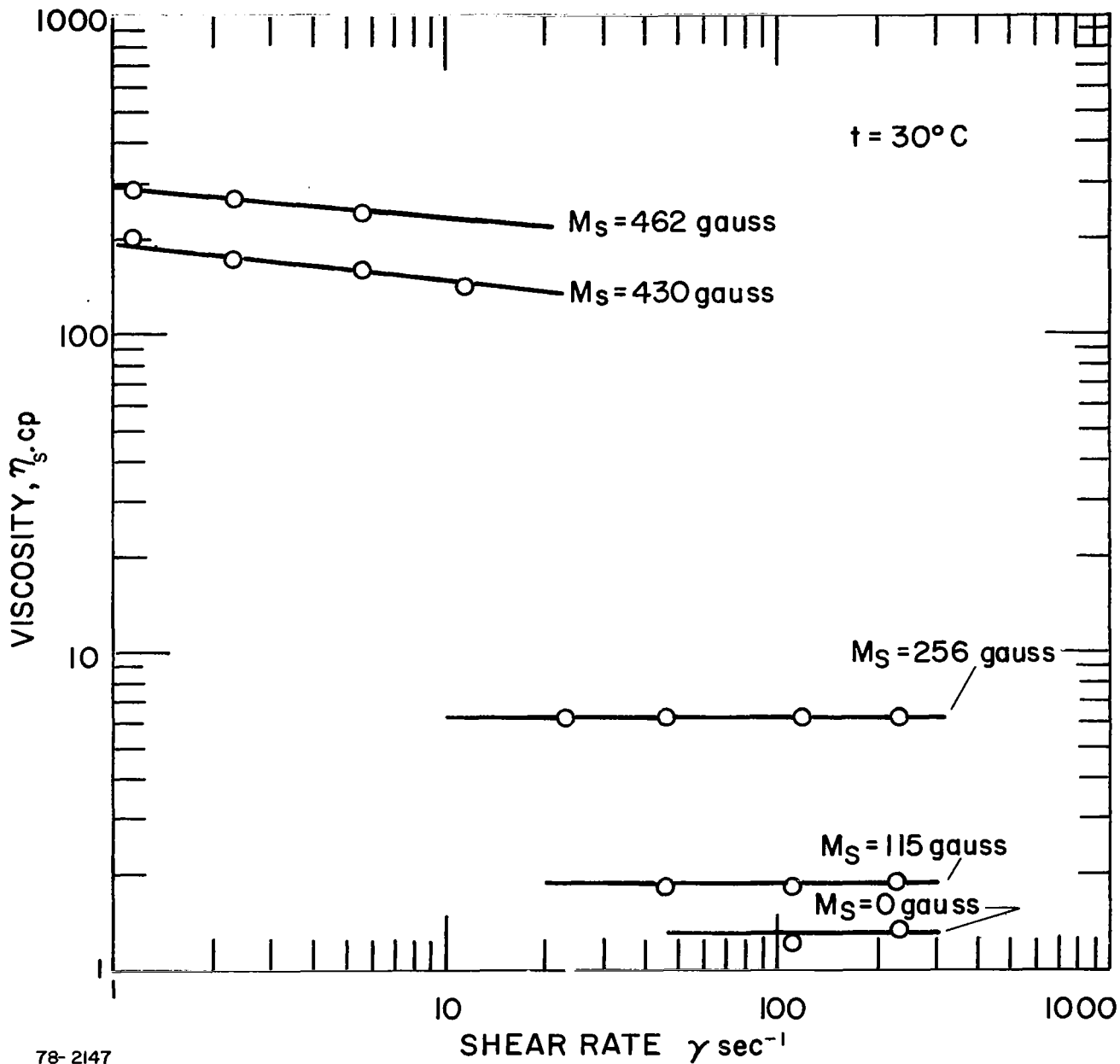
Figure 14 VISCOSITY OF WATER BASE FERROFLUID 1048 AS A FUNCTION OF SHEAR
RATE AND SATURATION MAGNETIZATION

In the above equation, ϕ_c is a critical concentration at which the fluid becomes rigid because of close packing of the particles. As was reported previously, (ref. 28) $f(\phi_c) = 1.55 \pm 0.05$ for $0.7 \leq \phi_c \leq 1$. One usual assumption is to treat a suspension as a system of equal sized spheres that becomes rigid when it assumes a hexagonal close packed configuration ($\phi_c = 0.745$).

By assuming each particle in suspension to be surrounded by a rigid stabilizing layer, the volumetric solids concentration, ϵ_D, is related to ϕ by the ratio of the thickness of the stabilizing layer, δ, to the particle diameter, D. For equal sizes non-interacting spheres this ratio is

$$\frac{\phi}{\epsilon_D} = \left(1 + \frac{2\delta}{D}\right)^3 \tag{17}$$

while for spherical particles of varying sizes, the following expression is used:

$$\frac{\phi}{\epsilon_D} = 1 + \frac{6\delta}{\overline{D}_{SA}} + \frac{12\delta^2}{\overline{D}_{SA}\overline{D}_{LA}} + \frac{8\delta^3}{\overline{D}_{SA}\overline{D}_{LA}\overline{D}_{NA}} \tag{18}$$

where:

$\overline{D}_{NA}$ = number mean diameter

$\overline{D}_{LA}$ = length mean diameter

$\overline{D}_{SA}$ = surface mean diameter

Substituting Eq. (17) into (16) and transposing terms leads to the following equation for a ferrofluid

$$\frac{\eta_s - \eta_o}{\eta_s} = 2.5\psi\epsilon - 1.55(\psi\epsilon)^2 \tag{19}$$

where $\psi = \dfrac{\phi}{\epsilon} = f(D, \delta)$

As discussed in the magnetization section,

$$M_H = KM_d \epsilon_D \tag{20}$$

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Substituting equation (20) into equation (19), the following equation for the viscosity of a ferrofluid is obtained:

$$\frac{\eta_s - \eta_o}{\eta_s} = \frac{M_H}{K\,M_d}\left(2.5\,\psi\ -1.55\,\psi\ \frac{M_H}{K\,M_d}\right) \qquad (21)$$

According to this equation, fluid viscosity, η_s, will depend on domain magnetization, conversion and a function of the ratio of δ/D as well as on M_H and η_o, the parameters explicitly expressed in Figure 13.

This equation also shows that it is not possible to predict the variation of η_s with M_H unless ψ is known. This entails a knowledge of the thickness of the stabilizing layer, δ, and of particle diameter. It is possible to measure D directly, but it is not possible to measure by any direct means.

However, Equations (19) or (21) are useful as a means of estimating the thickness of the stabilizing layer surrounding the particles since all the other terms but ψ can be measured directly. Using ϵ_D as a measure of solids concentration, if Equation (19) is obeyed, a plot of $\frac{1}{\epsilon_D}\left(\frac{\eta_s - \eta_o}{\eta_s}\right)$ versus ϵ_D should yield a straight line whose intercept should be numerically equal to ψ. If the particle distribution is known, then can be calculated from Equation (18).

The viscosity data from Figure 10 was plotted in this manner for each fluid to obtain a value of ψ. These results are presented in Table 7 together with the values of $\overline{D}_{SA}$, $\overline{D}_{LA}$ and $\overline{D}_{NA}$ obtained from electron micrographs for each fluid. In each case a value of δ can be calculated from these values by a trial and error procedure from Equation 18. These results are also presented in Table 7.

For the kerosene/Tenlo 70 systems in which the particle distributions differ greatly, the calculated values of δ agree to within 10%, which can be accounted for by deviation of 10% in the determination of the average particle size. A value of 38 Å $\pm$ 2 Å was found for these systems. Tenlo 70 was the surfactant that produced the smallest value of δ in kerosene to date.

The value of ψ obtained for fluorocarbon base fluid 1042 was 4.1 and the value of δ equal to 40 Å. Structural models of the HFPO polymer acid molecules show them to be rigid molecules in which the length of a mer unit is about 4 Å. The length of an HFPO decamer acid molecule should be approximately 40 Å. which is in agreement with the value of found above.

The values of ψ obtained for water base fluid 1048 was 9.0. This is a higher value than for any of the other fluids examined. The value of δ obtained in this instance is 84 $\overset{o}{A}$. This value is higher than the values obtained to date in either hydrocarbon or fluorocarbon systems. One possible explanation is that the stabilizer Aerosol C-61 is a bulky molecule which occupies a large volume. Another possibility is that it is electrically charged so that the mechanism of repulsion in this case is one of ionic repulsion rather than of entropic repulsion. The ionic double layers developed in this case could be thicker than the solvated layer due to non-ionic species.

Table 7 - STABILIZING LAYER THICKNESS FOR SELECTED FERROFLUIDS

Fluid No.	G44	1032	1042	1048
Carrier Liquid	Kerosene	Kerosene	Freon E-3	Water
Stabilizer	Tenlo 70	Tenlo 70	HFPO Decamer acid	Aerosol C-61
ψ	4.0	3.2	4.1	9.0
$\bar{D}_{SA}$ $\overset{o}{A}$	105	190	162	178
$\bar{D}_{LA}$ $\overset{o}{A}$	91	136	100	140
$\bar{D}_{NA}$ $\overset{o}{A}$	78	100	63	110
δ $\overset{o}{A}$	36	40	40	84

Preparation of Magnetic Fluids of Low Viscosity

Introduction. - The information concerning δ, the stabilizing layer thickness for different solvent/surfactant systems, was used to prepare magnetic fluids of increased saturation magnetization and lower viscosity. The magnetization of a fluid increases as volume concentration of the core solids:

$$M_H = KM_d \epsilon_D \qquad (20)$$

The viscosity increases as a function of the volume concentration of solvated solid particles, ϕ. It is desirable to make the ratio $\dfrac{\phi}{K \epsilon_D} = \dfrac{\psi}{K}$ as small as possible since the solvated layer does not contribute

to the magnetic response. ψ increases as a function of δ/D and K increases as D. Therefore, in order to increase the magnetization of a fluid (at a constant viscosity level) it is desirable to decrease δ and increase D as much as possible. However, it will be recalled from stability considerations discussed in the first section that there is a minimum value of /D required to maintain particle stability and that this minimum increases rapidly with increasing D.

The problem of preparing a ferrofluid with a high magnetic moment reduces the following:

1. Finding a solvent-surfactant system which results in as small a value of δ as possible, and

2. Preparing a ferrofluid in this system in such a manner that only the largest particles which are stable remain in suspension. The resulting ferrofluid presumably contains no small particles which would have an inefficient ratio of δ/D and evidently no non-magnetic particles.

Choice of Systems. - Based on examination of the viscosity-magnetization data and particle size distribution data, the kerosene base fluids which exhibited the smallest stabilizing layer thickness were Tenlo 70 stabilized suspensions for which a value of $\delta = 40$ Å was determined. Most of the work in trying to increase fluid magnetization was done with kerosene-Tenlo 70-magnetite colloids.

In addition, limited work was also done with HFPO hexamer acid stabilized dispersions in Freon E-3 for which a value of $\delta = 30$ Å was found.

Method of Decreasing δ. - Since grinding is a random process which generates particles with a distribution of diameters and can also result in non-magnetic occlusions due to wear of balls and/or mills, a beneficiation step is needed to obtain improved fluids. This beneficiation operation has to separate the desirable large magnetic particles from smaller particles and from non-magnetic particles irrespective of size. The two classification techniques used were centrifugation and magnetic dialysis which were already discussed.

Tenlo 70-Kerosene Magnetite Systems. - The viscosity as a function of magnetization for different Tenlo 70-kerosene magnetite base ferrofluids are presented in Figure 15. Included are Fluids G44 and 1032, already presented in Figure 13; Fluids 1068, 1069, 1070, 1071 which are the feed
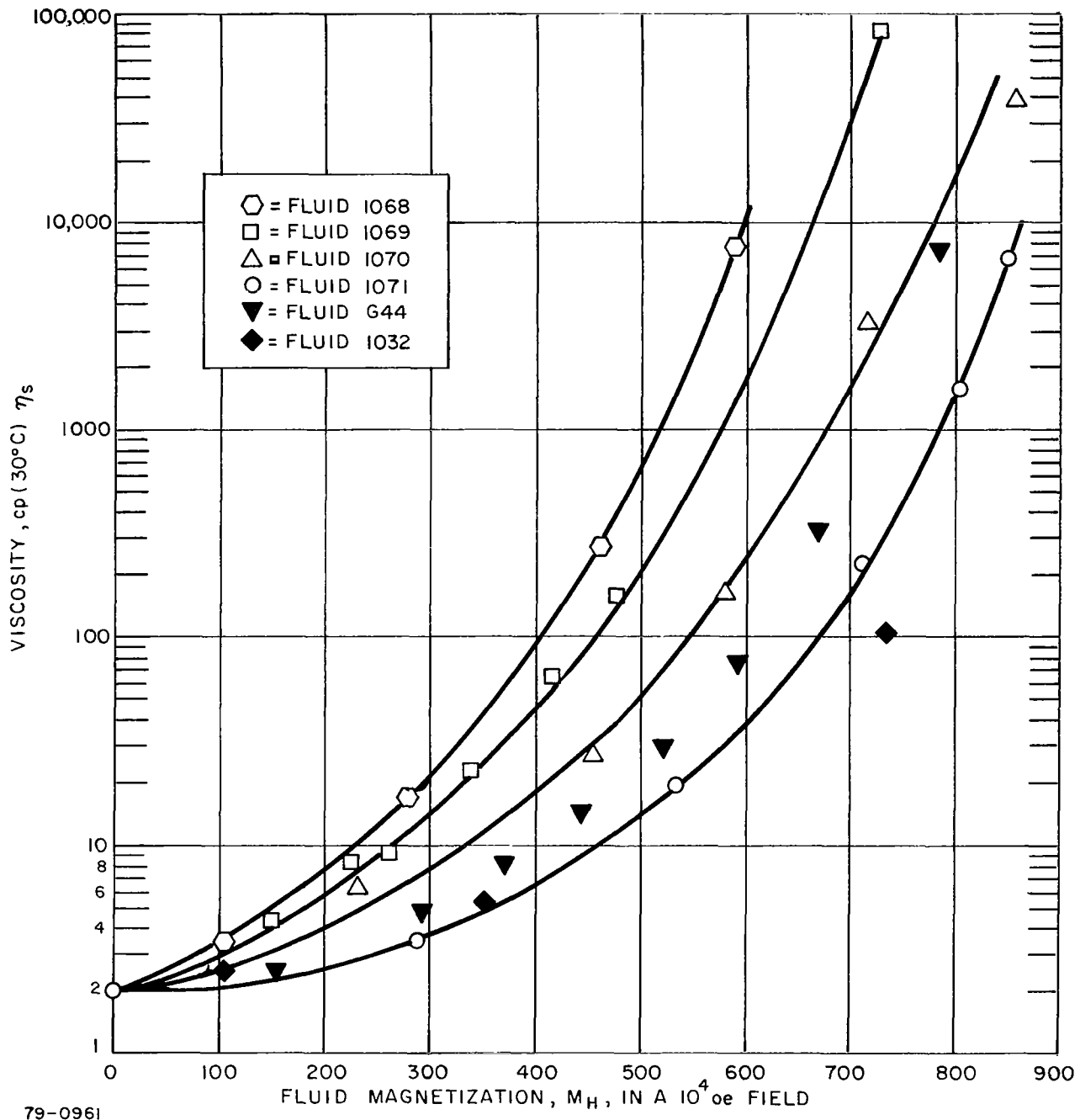
Figure 15 VISCOSITY/MAGNETIZATION PROPERTIES OF TENLO 70 STABILIZED
HYDROCARBON FERROFLUIDS

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and product liquids of one, two and three stage dialysis experiments. Two indices were available to measure average particle size M_L/M_H and $\bar{D}$ obtained from electron micrographs These values are presented in Table 8.   The viscosity of a ferrofluid increases more rapidly with saturation magnetization as the particle size decreases. The most successful attempt at preparing a high magnetization fluid with this solvent/surfactant system were fluids 1032 and 1071. The improved viscosity characteristics are due to a marked increase in particle size over the other fluids.

Table 8 - VISCOSITY PARAMETERS FOR TENLO 70/KEROSENE/MAGNETITE SYSTEMS

Fluid	G44	1032	1068	1069	1070	1071
M_L/M_H	0.29	0.42	0.22	0.24	0.31	0.34
$\bar{D}$ (from Fig. 10) $\mathring{A}$	118	136	100	106	120	125
K (conversion)	0.745	0.75	0.68	0.70	0.73	0.71
ψ	4.91	3.60	6.56	5.65	4.80	4.04
δ/D (from Eq. 17)	0.35	0.27	0.44	0.39	0.34	0.30
δ, $\mathring{A}$	41	37	44	41	41	38
M_M^* ($\phi_c = 0.745$) gauss	635	746	440	520	640	740
M_M^{**} ($\phi_c = 1.00$) gauss	854	1000	590	710	860	990
M_H' (expt) gauss	784	735	589	730	858	850
@ η 30 cp	7400	102	7800	84000	39000	6600

Table 9 - VISCOSITY PARAMETERS FOR

HFPO HEXAMER ACID/FREON E-3/MAGNETITE SYSTEMS

Fluid	1045	1046
M_L/M_H	0.14	0.22
$\overline{D}$ (from Fig. 10) $\overset{\circ}{A}$	88	105
K (conversion)	0.53	0.63
ψ	5.10	3.98
δ/D (from Eq. 17)	0.36	0.29
δ $\overset{\circ}{A}$	32	30
M_M^* ($\phi_c = 0.745$)	440	670
M_M^{**}($\phi_c - 1.00$)	590	900
M_H' (expt) gauss	510	612
@ η 30 cp	102	250

Values of ψ were obtained from the viscosity data for each of the fluids. A value of $\overline{D}$, the average particle diameter, was obtained for each of the fluids from magnetization measurements M_L and M_H from the plot in Figure 10. Substituting these values into Equation 17 allows to be calculated in each case. The method is different and not as correct as the one described in the previous section since no account of particle size distribution is taken. It is, however, gratifying to note that the value of δ is essentially the same in all cases.

It is of interest to compare the magnetization of the most concentrated ferrofluid actually prepared in each case, M_H', to the most concentrated ferrofluid that could be theoretically prepared. This maximum magnetization, M_M, occurs at ϕ_c when the system becomes rigid and it is not possible to incorporate more particles into the suspension. M_M can be expressed as follows:

$$M_M = \frac{K\ M_d\ \psi}{\phi_c}$$

One assumption is that the fluid becomes rigid and further concentration is not possible once the particles have been achieved a hexagonal close packed configuration: $\phi_c = 0.74$. Call the corresponding maximum magnetization M_M^*. Another assumption is to consider that the solvated layer can deform so that the system can approach a value of $\phi_c = 1$. Call the corresponding value of maximum magnetization M_M^{**}. Calculated values of M_M^* and M_M^{**} are also presented in Table 8. In all cases values of M_H' are greater than M_M^* and approach M_M^{**}. This finding indicates that the stabilizing layer around the particles is deformable and in concentrated systems there is little free liquid. This deformation of particles which occurs during flow accounts for the non-Newtonian behavior observed at high concentrations and reported in Figure 14.

It is possible to question the validity of Equation (19) since the fluids do show evidence of non-Newtonian behavior. It is to be pointed out that in these systems, while η_s is a function of shear rate, the value of $\dfrac{\eta_s - \eta_o}{\eta_s} \longrightarrow 1$ for all obtained values of η_s in this range.

Furthermore, the characteristic function of ϕ_c, which is a coefficient in Equation (19), is essentially invariant for all values of ϕ_c greater than 0.70. At a value of $z = 1$ of the curves in Figure 1, it is possible to calculate the maximum size of a particle that is stable for a given stabilizing layer thickness δ. For $\delta = 40$ Å, which corresponds to the value found for Tenlo 70/kerosene system, the critical value of D is 120 Å. This is slightly less than the average particle size found for fluid 1032 ($\overline{D} = 136$ Å). This larger experimental particle size is

interpreted to reflect the fact that the individual particles are partially demagnetized which lowers the magnetic attraction between two spheres. The ratio $\left[\dfrac{120}{136}\right]^3$ is 0.68 which approaches the conversion K = 0.74 found for 1032. This finding further suggests that it would be difficult to obtain Tenlo 70 stabilized systems of greater particle size. This sets the value of M_M^* for 1032 as the maximum limiting magnetization of any kerosene produced to date. Magnetically stronger fluids would require a smaller value of δ

HFPO Hexamer Acid - Freon E-3 Magnetite Systems. - Of the fluids prepared during the course of the present program, the only surfactant-solvent system which resulted in a thinner stabilizing layer than Tenlo 70/kerosene was the HFPO hexamer acid/Freon E-3 system. The viscosity-magnetization curve for this fluid is presented in Figure 16. This fluid was magnetically dialyzed to yield a small quantity of Fluid 1046 whose viscosity/magnetization curve is also presented in Figure 16. The value of δ for this system is slightly less than 30 Å. This is 25% less than the value found with the HFPO decamer system. There is not a one to one accord between stabilizing layer thickness and molecular weight of surfactant. This is most probably due to the presence of Freon E-3 solvent molecules. The values of the different parameters of interest for these fluids are presented in Table 9. From Figure 1, the maximum size particle that can be stabilized by a value of δ = 30 Å is about 105 Å. For fluid 1046, $\bar{D}$ = 80 Å. It is evident, therefore, that the full potential of this system has not been fully explored. Values of $M_M^* \simeq 1000$ gauss are possible with this system if subjected to extensive separation and a value of K = 0.70 is obtained.

Preliminary results with higher HFPO acids indicates that δ increases with molecular weight for this system.

The possibility of preparing ferrofluids with smaller values of δ in Freon E-3 exists because there are lower molecular weight HFPO acids available which have not yet been used in the grinding tests. The minimum molecular weight needed to stabilize magnetite particles has not yet been determined. This could be done by systematically preparing grinds with HFPO pentamer acid, HFPO tetramer acid, HFPO trimer acid, etc. in Freon E-3 or a lower molecular weight homologue until a system is found that does not result in peptization. This sets the lower limit of δ and also the maximum magnetization that could be attained.

Viscosity of a Ferrofluid in a Magnetic Field

The novelty of the magnetic fluid dispersions developed is that they retain their liquid characteristics in an applied magnetic field.
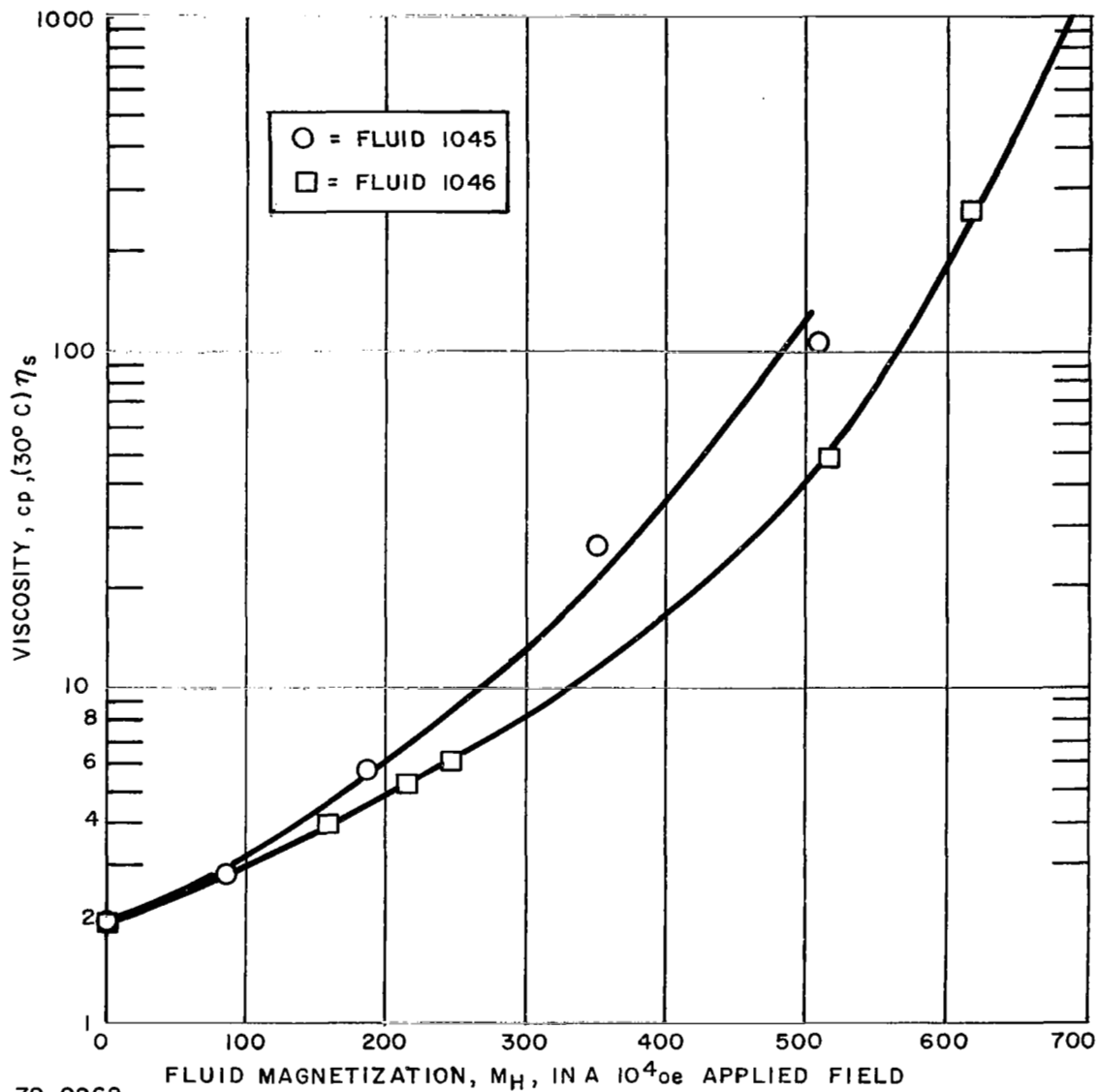
Figure 16 VISCOSITY/MAGNETIZATION PROPERTIES OF HFPO HEXAMER ACID
STABILIZED FLUOROCARBON FERROFLUIDS

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No quantitative measure of the effect of a magnetic field on suspension viscosity had been reported. Measurements of fluid viscosity as a function of applied magnetic field and shear rates were made during the course of the program.

The experiments consisted in measuring the effect of a vertical magnetic field on the viscosity of a thin layer of ferrofluid sheared in a horizontal direction without any overall fluid displacement. The viscosimeter used was the modified Wells-Brookfield cone/plate viscometer that was already described. After some preliminary low field measurements at Avco, a first series of measurements were made at the Francis Bitter National Magnet Laboratory of the Massachusetts Institute of Technology in Cambridge, Mass. These measureements were made with a variety of ferrofluids at shear rates that were varied between .035 and 230 sec^{-1} and in magnetic fields as high as 21 kilo-oersted.

An increase in suspension viscosity was observed under certain conditions. This can be expressed as:

$$\frac{\eta_H}{\eta_s} = f\left(\frac{\gamma\,\eta_o}{M\,H}\right) \qquad (21)$$

where:

η_H = viscosity of the suspension in an applied magnetic field, H, poise

η_s = viscosity of the suspension in the absence of a magnetic field, poise

η_o = viscosity of the carrier liquid, poise

γ = shear rate, sec^{-1}

M = fluid magnetization, gauss

The controlling parameter is the dimensionless ratio of viscous stress to magnetic stress.

The above experiments and the dimensionless analysis approach used to correlate the data are described in more detail in an article accepted for publication(ref. 29). The principal results are presented in Figure 17 where η_H/η_s is plotted against $\frac{\gamma\eta_o}{M\,H}$. From this figure it was concluded that there are three ranges:
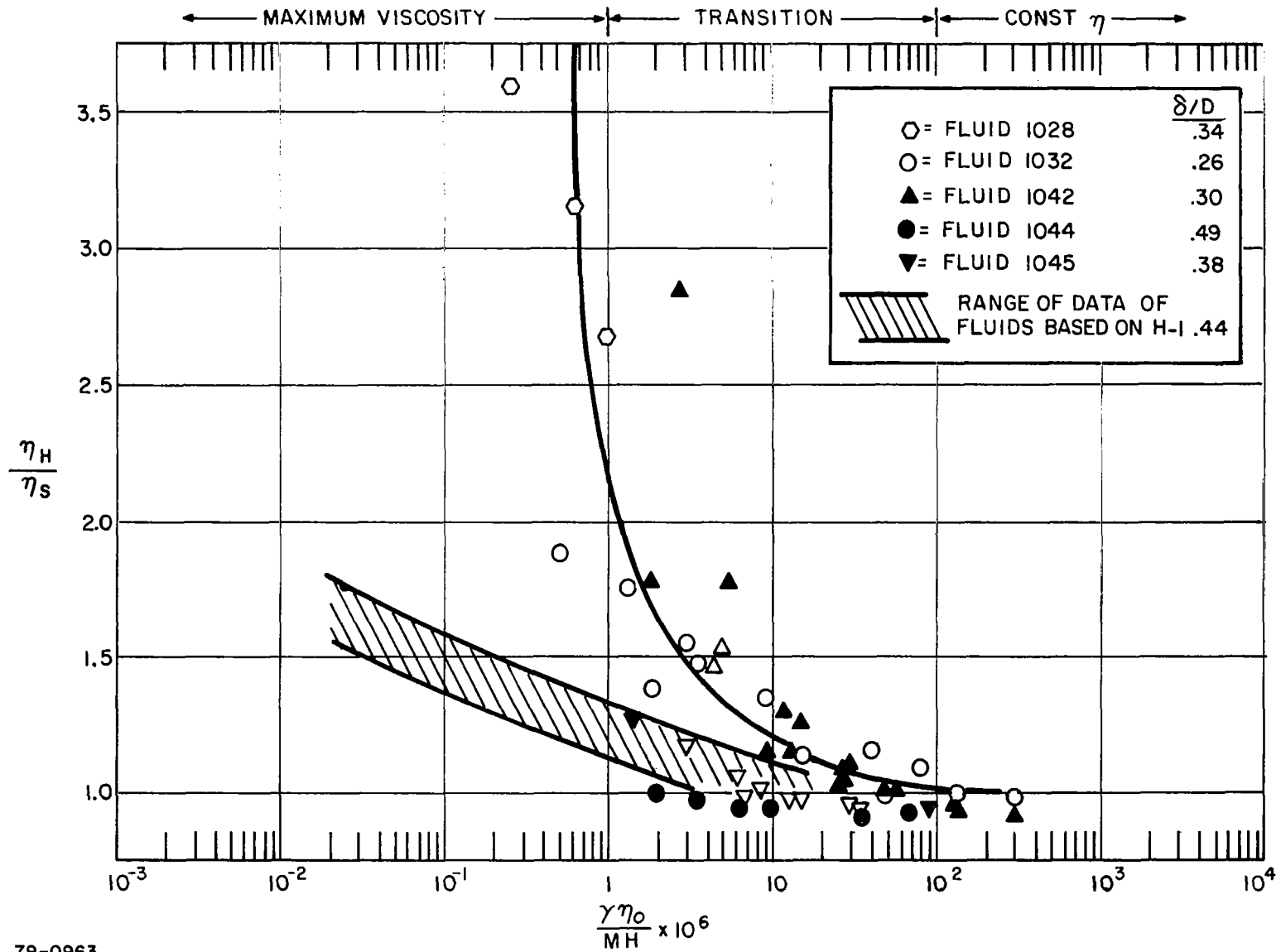
Figure 17 EFFECT OF A MAGNETIC FIELD AND SHEAR RATE ON THE VISCOSITY
OF A MAGNETIC FLUID

$$0 < \frac{\gamma \eta_o}{M\ H} < 10^{-7} \qquad \text{Viscosity is constant at maximum value,}$$

$$10^{-7} < \frac{\gamma \eta_o}{M\ H} < 10^{-5} \qquad \text{Viscosity is dependent on field and shear rate,}$$

$$10^{-5} < \frac{\gamma \eta_o}{M\ H} < \infty \qquad \text{Viscosity is constant at minimum value}$$

Further measurements were made at higher fields (as high as 75 Koe) in order to obtain data in the region $\frac{\gamma \eta_o}{M\ H} < 10^{-7}$. These were made with products of grind H-1 (Tenlo 70 - kerosene-magnetite) in which the particle concentration was varied to attain a ten-fold variation in M and the carrier liquid was varied (kerosene, mineral oil, silicone L43) to attain a variation of carrier liquid viscosity of over three orders of magnitude. Difficulties in obtaining data at high fields in the air solenoid were encountered because of the presence of horizontal gradients which tended to push the fluid away from the sensing head of the instrument. Fluid migration could be controlled by inserting an iron cylinder underneath the viscosimeter which would concentrate the field in the center.

With concentrated dispersions there was the additional problem of spike formation at high fields. Instead of having a uniform layer of liquid the fluid would collect into discrete cone-like structures (ref. 5). Very high field measurements were taken only with dilute fluids ($M_H < 120$ gauss).

The reduced data from these measurements are also presented in Figure 17. They essentially all fall on the same curve. The transition of fluid viscosity to a shear rate and field dependent regime occurs at a value of $\frac{\gamma \eta_o}{M\ H}$ of about 10^{-6} which is one order of magnitude lower than the value previously reported. Even though measurements were made at values of $\frac{\gamma \eta_o}{M\ H} \longrightarrow 10^{-2}$, values of $\frac{\eta_H}{\eta_s} \longrightarrow 4$ were not obtained.

It appears, upon re-examining the data presented in Figure 17, that there is an additional parameter that was not previously included in the dimensionless analysis. This is the dimensionless ratio δ/D where δ is the thickness of the solvated stabilizing sheath around a particle and D is the diameter of the magnetic core. The hydrodynamic properties of a particle will depend on its overall volume, which is a function of D and δ, whereas the magnetic properties of a particle are a function of D alone.

Values of δ/D obtained for each of the fluids from viscosity data and Equations (17) and (19), are also presented for each of the fluids in Figure 17. The data indicate that as the ratio δ/D increases, a smaller value of $\dfrac{\gamma\eta_0}{MH}$ is needed to cause a given increase in $\dfrac{\eta_H}{\eta_s}$. The viscosity of a magnetic fluid becomes less sensitive to an applied magnetic field as δ/D increases.

Figure 18 presents the effect of δ/D on $\dfrac{\eta_H}{\eta_s}$. The solid curves are based on the best data available data. They include the range of the values of δ/D of interest. There is a lower limit of $\delta/D > 0.2$ because of the particle-to-particle interactions discussed in Figure 1 and the empirical knowledge as to the minimum thickness of the stabilizing shell that can be developed. There is no theoretical upper limit to δ/D. However, since the saturation magnetization of the suspension decreases as a cubic function of δ/D, there is little interest in systems for which $\delta/D > 0.5$.

These results indicate that the value of $\dfrac{\gamma\eta_0}{MH}$ at which there is a transition from a constant viscosity term to one which is shear rate and field dependent decreases with decreasing δ/D. The range of values of $\dfrac{\gamma\eta_0}{MH}$ over which $\dfrac{\eta_H}{\eta_s}$ is shear rate and field dependent also increases with decreasing δ/D. The values $10^{-7} < \dfrac{\gamma\eta_0}{MH} < 10^{-5}$ for the transition range is characteristic of most ferrofluids prepared, which typically have a value of $\delta/D \approx 0.35$.

DIELECTRIC CONSTANT OF FERROFLUIDS

The dielectric properties of a ferrofluid become of importance in electro-mechanical applications such as inertial sensors.

Dielectric constant was measured for several ferrofluid systems using an axisymmetric projected field capacitance probe. The effort was divided into four parts,

1. Probe calibration using standard liquids,

2. The measurement of dielectric constant of surfactant solvent systems used in ferrofluids,
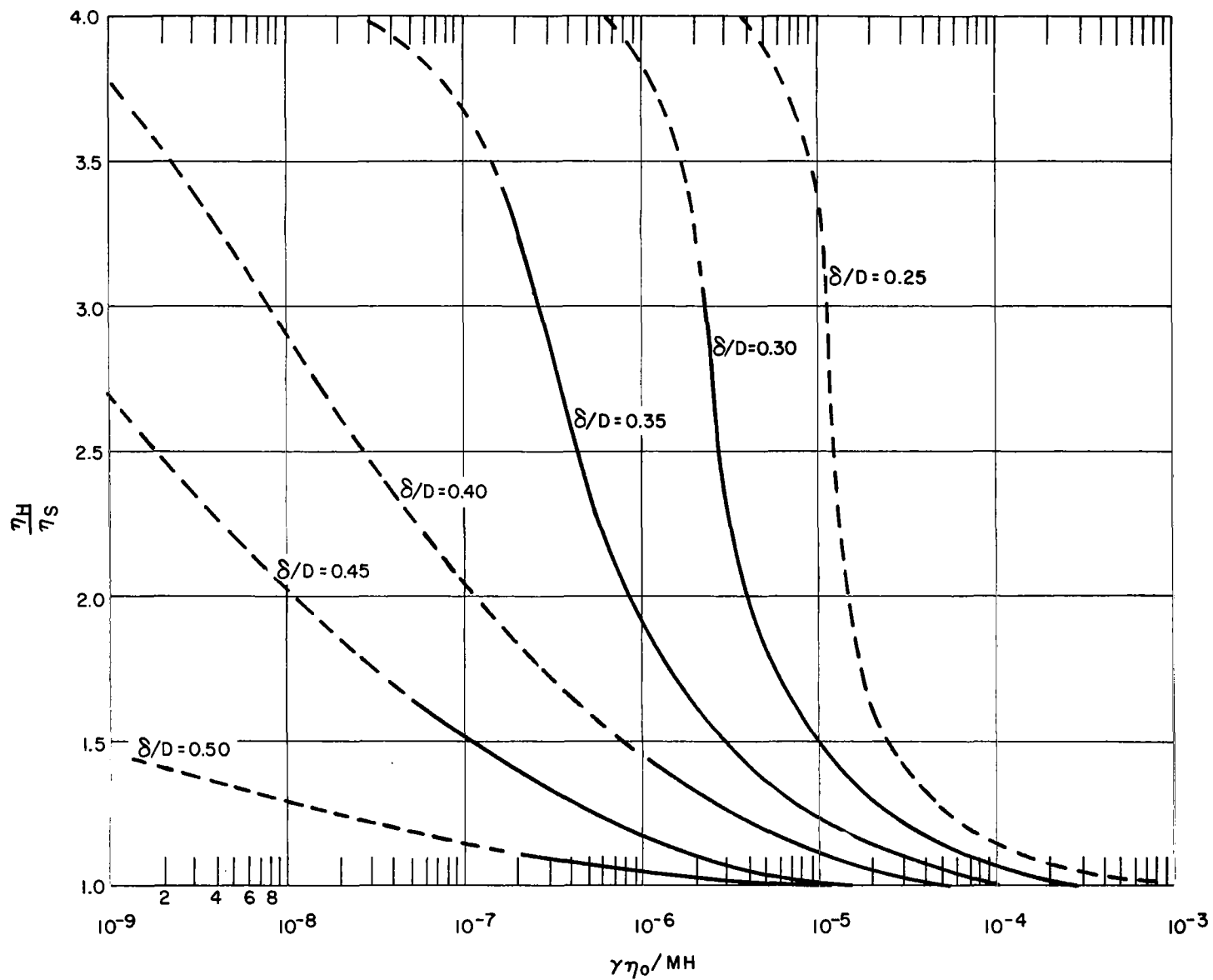
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Figure 18 EFFECT OF δ/D ON THE VISCOSITY OF A MAGNETIC FLUID IN A
MAGNETIC FIELD

3. A study of the dielectric constant ferrofluid system with varying solids concentration,

4. The study of dielectric constant under the influence of an applied magnetic field.

Apparatus. - An axisymmetric projected field probe with a 2-inch diameter active face area, and an effective depth of field of 0.1 inches was used. A sample cup was made by covering the open bottom of glass ring 2-inches inside diameter and 1-inch high with Saran Wrap. The Saran Wrap was held in place with a rubber band around the ring. The presence of the sample cup in the probe field had negligible influence on the probe capacitance. The relative capacitance, was obtained on a General Radio Automatic Capacitance Bridge, at 400 and 1000 Hz, and converted to dielectric constant using the calibration curves discussed below.

Probe Calibration. - The configuration of the probe used is rather complex so simple calibration factors are applied to obtain the true values of the dielectric constant. To calibrate the probe, the relative capacitance of several standard liquids was measured at 1000 Hz and 400 Hz. The measurements for several liquids was reported in Figure 19. No attempt was made to determine the purity of the samples; perhaps this is the reason for the scatter of data. The static data was obtained from NBS circular 415, (ref. 30) the data at 1 KHz from von Hippel (ref. 31).

The calibration reported here does not strictly apply for magnetic dielectrics since the probe actually responds to the complex impedence of the fluid. Further measurements are needed to uniquely determine the values of the real and imaginary parts of the dielectric constant and permeability.

Surfactant-Solvent Systems. - Three systems were studied. In the first system, the surfactant was oleic acid and the solvent was kerosene. In this system the surfactant concentration varied from 0 to 100% by weight of oleic acid. The dielectric constant was 2.9 + 0.1 over the entire range of concentration. For the second system, the surfactant was ENJAY 3854 and the solvent xylene. The surfactant concentration varied from 0 to 50% by weight ENJAY 3854. The dielectric constant was 2.6 + 0.3 over the range of concentration. For the third system, the surfactant was Tenlo 70, the solvent kerosene. The concentration varied from 0 to 100% by weight Tenlo 70. In this system the dielectric constant changed by nearly 2 orders of magnitude. For a 0.3% solution the dielectric constant was 2, for a 1.0% solution the dielectric constant was 120. The dielectric constant of 100% Tenlo 70 was 60.
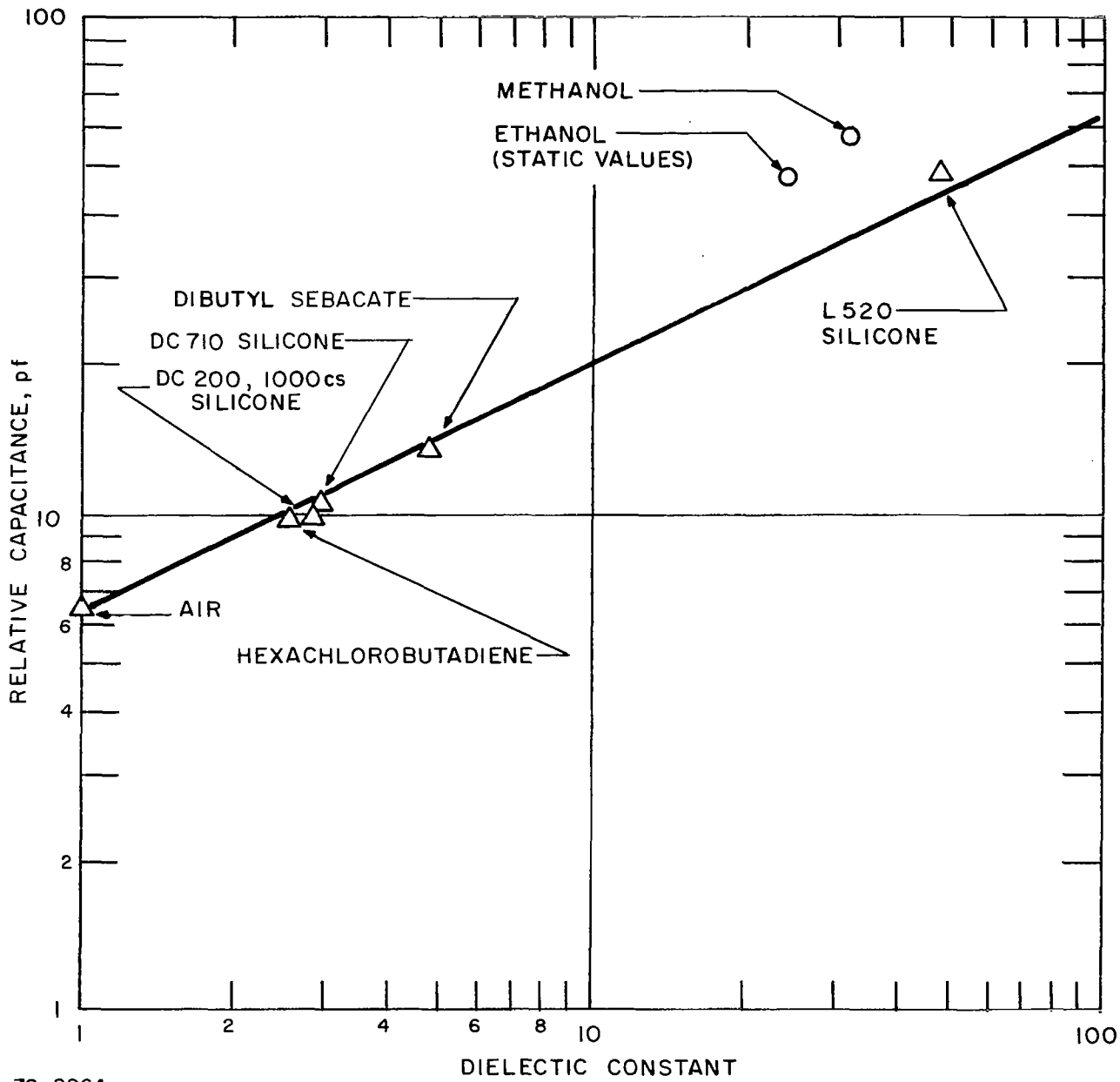
Figure 19 CALIBRATION OF PROBE WITH STANDARD LIQUIDS AT 1 KHZ

79-0964

Ferrofluid Systems. - Two ferrofluid systems were studied. In both cases the solvent was kerosene. In the first case the surfactant was oleic acid (G72); in the second case the surfactant was Tenlo 70 (H1). For both systems the dielectric constant appeared to be a function of the volume percent of total solids present, as seen in Figure 20. The dielectric constant increases rapidly from zero loading, a dielectric constant of 2 corresponding to kerosene to about 50 with a 4% solids loading. As the loading is further increased, the dielectric constant approaches that of the magnetite powder. A dielectric constant of 15 was measured for a sample of compacted magnetite powder. It is supposed that for the system H1 containing Tenlo 70 the amount of free Tenlo 70 in solution must be much less than 1% since the dielectric constant does not reach the value of 120 in this system.

To further explore the generality of the relationship of Figure 20 the dielectric constants of a variety of ferrofluids were measured. Systems containing oleic acid in decane, and fluorocarbon surfactant in a fluorocarbon carrier follow the same dependency as by the kerosene systems.

It is worth noting that the loss tangent of the ferrofluid systems was an order of magnitude greater than for kerosene.

Magnetic Field. - An attempt was made to measure the dielectric constant of ferrofluids in the presence of a magnetic field. A difficulty was deformation of the free ferrofluid surface in the presence of the magnetic field. The deformations were minimized by using weak fields. In all the observed cases increase of dielectric constant was less than 5%.

For a magnetic field perpendicular to the liquid surface, a field of 1.4 kilo-oersted was used for a 100 gauss fluid (G72). The dielectric constant increased by 2%. For a 310 gauss fluid (G72) the field was limited to 0.30 kilo-oersteds to avoid spike formation, the dielectric constant increased by 3%.

For a magnetic field parallel to the liquid surface for a ferrofluid of 40 gauss (G72) the field was 4.3 kilo-oersted; the increase of dielectric constant was 5%. For stronger fluids the free fluid surface deformed under the influence of field non-uniformities, thus for 340 gauss fluid (G72) a field of 0.4 kilo-oersted was used; the dielectric constant increased by 1%.

Thus it is seen that the presence of the magnetic field results only in a minor increase in dielectric constant. To extend the range of the measurements closed fluid sample holders could be employed to allow the use of high magnetic fields without affecting the sample geometry.
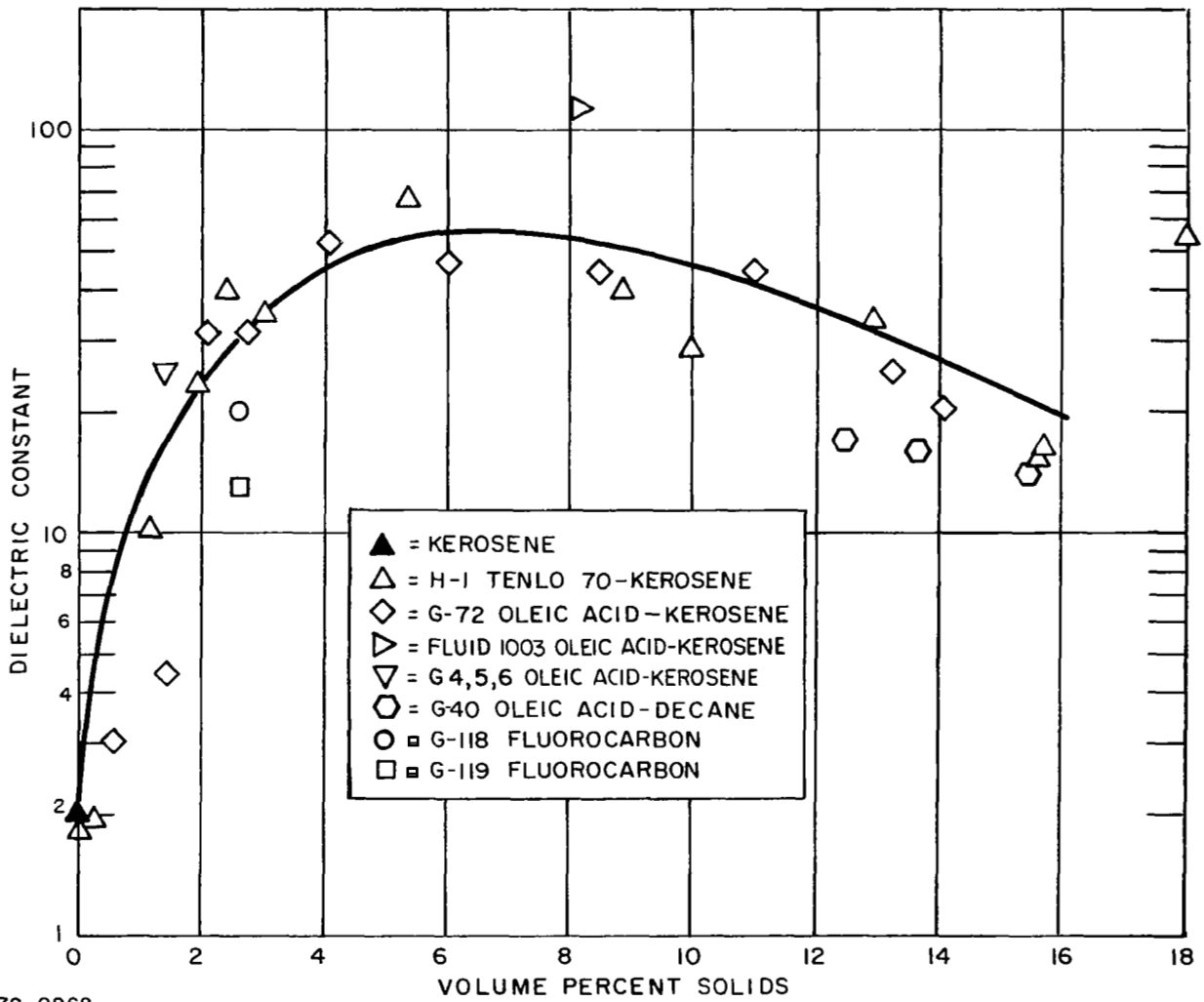
Figure 20 DIELECTRIC CONSTANT OF FERROFLUID SYSTEMS AT 1 KHZ

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THERMALLY STABLE FERROFLUIDS

Thermal Testing of Different Ferrofluids Prepared Under Program

Introduction. - All the ferrofluids prepared before the initiation of the present program had severe temperature limitations. The best fluid prepared then flocculated when heated to a temperature of 140°C. Many applications, and especially energy conversion, require a fluid that remains stable to at least 140°C and preferably over a much wider range of temperature such as -40°C to 300°C.

The stability of the ferromagnetic colloidal dispersions is due to the presence of an adsorbed surfactant at the surface of the particles in suspension which results in the formation of a stabilizing layer. High temperature induced flocculation of the sol is believed due to desorption of the surfactant at elevated temperature due to increased thermal motion or to disruption of the stabilizing film. Higher temperature stability should be obtained with either a molecule that bonds more firmly to the surface of the particles or by preventing molecules from leaving the surface even if desorption occurs.

Experimental Methods and Results. - A number of the many different ferrofluids prepared during the course of the present phase of the program were subjected to extensive exposure to high temperatures.

These tests are a continuation of the thermal testing program initiated in Phase I. In addition to the visual observations that were recorded in Phase I, attempts were made to obtain more quantitative measures of fluid stability. Where there were no very drastic physical changes (such as extensive separation or gellation), saturation magnetization and/or viscosity measurements on the fluid samples at room temperature, were performed on the ferrofluid samples before and after the individual tests.

A list of all the materials exposed to thermal testing is presented in Table 10. This table lists code numbers, original grind numbers (where applicable), the solvent and the surfactant used. All the ferrofluids used were magnetite suspensions.

In these tests, samples of ferrofluids were sealed in glass ampoules which were then heated at temperature for a given period of time. Three series of tests were performed by immersing ampoules in an oil bath maintained at test temperature. Test conditions were:

Table 10 - MATERIALS SUBJECTED TO THERMAL TESTING

Identification Code	Original Grind Number	Carrier Liquid	Stabilizing Agent
1005	G58	Kerosene	Oleic acid
1011	G80	Glycerol	Tamol 731
1020	G77	Kerosene	Tenlo 70
1030	G64	Tetrahydro-naphthalene	Oleic acid
1035	G78/G79	L43	Tenlo 70
1038	G106	Dinonyl-phthalate	Triton X45
1041	G96	Lube oil	ENJAY 3854
G80B	G80	Water	Tamol 731
G96	G96	Kerosene	ENJAY 3854
G101	G101	Kerosene	ENJAY 3854
G103	G103	Kerosene	Octadecyl alcohol
G105	G105	Kerosene	Triton X35
G118	G118	E-3 Freon	HFPO decamer acid
G119	G119	E-3 Freon	HFPO hexamer acid

	Temperature	Time
Test No. 1	123°C	554 hours
Test No. 2	150°C	1080 hours
Test No. 3	186°C	340 hours

Subsequent testing at 260°C (500°F) for 160 hours and 315°C (600°F) for 24 hours on one ferrofluid that survived at 186°C was carried out by placing heavy walled ampoules (due to pressure build up) in a tubular electric furnace where temperature could be maintained to within 10°C.

These tests minimized or eliminated problems associated with evaporation of solvent and/or surfactant or reaction of solvent/surfactant with air at temperature under test. Some applications, however, require fluids exposed to air at elevated temperatures. Some samples, in test tubes open to atmosphere, were also immersed in the heating bath for different periods of time.

Development of a Thermally Stable Ferrofluid. - The findings of the thermal tests performed can be summarized by stating that only kerosene base ferrofluids stabilized with ENJAY 3854 surfactant are stable when exposed to prolonged heating at temperatures of 150°C or more. All the other fluids tested drastically changed properties. The results are summarized in Table 11.

In sealed systems, samples of products from grinds G96 and G101 essentially remained unchanged after exposure to 150°C for over 1000 hours or 186°C for 340 hours or 162 hours at 260°C, but flocculated after 24 hours at 315°C.

In open tube experiments, fluid 1041 which was obtained by vacuum evaporation of fluid G96 until no further observable evaporation occurred, lost weight continuously but at a decreasing rate. The weight loss which was about 8% per 100 hours at the start decreased to about a third of this value at the end of the test. This can be accounted for initially by loss of kerosene at the start of the test since all these compounds have a finite vapor pressure. The important finding is that flocculation did not occur so that from a colloidal point of view the system remained stable. These systems therefore satisfy one of the major objectives of the program.

ENJAY 3854 is one of a series of stabilizing agents developed by the ENJAY Chemical Company, a subsidiary of the Standard Oil Company of New Jersey, as additives for automobile lubricating oils. Finely divided lead oxide and carbon are by-products of the combustion of leaded gasoline

Table 11 - EFFECT OF TEMPERATURE ON THE STABILITY OF FERROFLUIDS

Test No.	1	2	3	4	5
Test Temperature, °C	123	150	186	260	315
Exposure Time, Hrs.	554	1080	340	160	24
Fluid					
1005	NT	U	U	NT	NT
1011	G	NT	NT	NT	NT
1020	S	U	U	NT	NT
1030	NT	U	NT	NT	NT
1035	S	U	U	NT	NT
1038	G	G	NT	NT	NT
G80B	G	NT	NT	NT	NT
G96	S	S	S	S	U
G101	NT	S	S	S	U
G103	S	S	U	NT	NT
G105	G	U	U	NT	NT
G118	S	NT	U·	NT	NT
G119	S	NT	U	NT	NT

S = Stable   NT = Not Tested

U = Unstable   G = Gel

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in automotive engines. These particles are removed from the cylinders by the lubricating oil and maintained in suspension by this additive. It is claimed that colloidal dispersions in lubricating oil will be stable to temperatures as high as 300°C. These materials are described in the patent literature (ref. 17, 18). These materials are derived from polybutene polymers containing from 500 to 1000 carbon atoms to which reactive polar groups such as carboxylic or amine groups have been added. The high temperature stability of the ferrofluids made with these dispersants is due to the polymeric nature of the surfactant. The molecule cannot only wrap itself around the particle but at the same time, the polar groups spaced on its polymeric backbone, can bond simultaneously with the particle surface. This lead to a more stable configuration than the formation of a stabilizing layer by many lower molecular weight molecules, any one of which is not restrained from leaving the surface by the presence of adjacent molecules. It is interesting to point out that on a particle with a surface area of 100 $\overset{o}{A}{}^2$ (D $\simeq$ 60 $\overset{o}{A}$) approximately 50 oleic acid molecules would be adsorbed since the cross-sectional area of an adsorbed molecule in a head to tail configuration is about 20 $\overset{o}{A}{}^2$. At the same time, the ratio of molecular weights of the active ingredient in ENJAY 3854 to that of oleic acid is about 50 as well. It is quite likely, therefore, that each particle in suspension in the layer system is coated with one stabilizing agent molecule.

The preparation of a thermally stable ferrofluid by adsorption of a polymeric molecule is similar in concept to the original proposal of preparing a thermally stable ferrofluid by surface polymerization of monomer molecules already adsorbed on the particle surface. As reported in a previous memorandum, (ref. 32) sulfur monochloride or sulfur dichloride was added to kerosene base ferrofluid stabilized by a multi-unsaturated fatty acid such as linoleic acid or linoleinic acid. Addition of sulfur chlorides always resulted in flocculation of the particles in suspension. There is evidence to believe that while surface polymerization occurred, as was desired, the resulting polymeric sheath was not solvated by the carrier which led to flocculation.

CONCLUSIONS

1. Novel ferrofluids have been synthesized which have the following principal characteristics:

    a. Higher concentration of magnetic colloid. This results in ferrofluid with a higher saturation magnetization and improved viscosity-magnetization characteristics.

b. Stability at temperatures as high as 500°F.

c. Incorporation in liquids such as water, glycol,
    esters and fluorocarbons. This results in
    ferrofluids which have a wide variety of
    properties.

2. The principal physical properties of a number of ferrofluids
    have been measured and correlated. The effects of domain
    magnetization of the suspended colloid, particle size,
    particle concentration, applied magnetic field and temper-
    ature on the magnetization of a ferrofluid have been
    measured and were found to be consistent with superpara-
    magnetic theory.

    The viscosity of ferrofluids has been measured over a
    range of fluid properties, shear rates and magnetic
    fields. These results have been correlated by physical
    models and dimensionless analysis.

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SYMBOLS

a   acceleration, cm/sec^{-2}

b   center to center particle distance, cm

g   acceleration of gravity = 981 cm/sec^{-2}

h   relative surface separation

k   Boltzmann's Constant = 1.38 x 10^{-16} $erg/^{o}K$

n   number of particles per unit volume

p   magnetic moment per particle

t   time, sec ; temperature, ^{o}C

v   particle volume, cm^{3}

z   stability criterion for magnetic colloid

A   Van der Waals attraction constant $\approx 10^{-12}$ erg

$\overset{o}{A}$ angstrom unit

C   constant

D   particle diameter

D_{c} critical particle diameter

$\overline{D}$ average particle diameter

$\overline{D}_{NA}$ arithmetic number average particle diameter

$\overline{D}_{LA}$ arithmetic length average particle diameter

$\overline{D}_{SA}$ arithmetic surface average particle diameter

$\overline{D}_{NG}$ geometric number average particle diameter

E_{L} London energy of interparticle attraction

E_{M} magnetic energy of interparticle attraction

E_R entropic energy of interparticle repulsion

H   applied magnetic field

K   magnetic conversion of colloid

K_1 grinding rate constant

M   magnetization

M_d domain magnetization

M_H high field magnetization

M_L low field magnetization

M_M ultimate saturation magnetization of a ferrofluid
           as viscosity $\longrightarrow \infty$

M_S saturation magnetization of a ferrofluid

S_g rate of particle sedimentation due to gravitational
           forces

S_M rate of particle sedimentation due to magnetic
           forces

T   absolute temperature

U   particle energy

$\overline{V}$ average particle volume

Y   unit dimension

Z   fractional conversion of colloid

γ shear rate

δ stabilizing film thickness

ϵ_D volume fraction solids in suspension from density
           measurements

ϵ_M volume fraction solids in suspension from
           magnetization measurements

η viscosity

η_o carrier liquid viscosity

η_s colloid viscosity

η_H magnetic colloid viscosity in a magnetic field H

μ micron = 1 micrometer

ξ thickness of non-magnetic mantle around a particle

ρ colloid density

ρ_C core particle density

ρ_O carrier liquid density

ρ_L liquid phase density

σ_G geometric standard deviation

ϕ volume fraction solvated solids

ϕ_C critical volume fraction solvated solids which results in a suspension of ∞ viscosity

ψ ratio of solvated volume to core volume