UNCLASSIFIED

AD NUMBER
AD879722
NEW LIMITATION CHANGE
TO Approved for public release, distribution unlimited
FROM Distribution authorized to U.S. Gov't. agencies and their contractors; Critical Technology; DEC 1970. Other requests shall be referred to Naval Weapons Center, China Lake, CA.
AUTHORITY
USNWC ltr dtd 30 Aug 1974

THIS PAGE IS UNCLASSIFIED

NWC TP 5061

COPY 64

FACTORS INFLUENCING THE MEASUREMENT OF THE YIELD STRESS OF GELS WITH A SPHERE RHEOMETER

by

Warren J. Murbach
Arnold Adicoff
Alan L. Woodman
Albert H. Lepie
Research Department

ABSTRACT. A forced vibration rheometer was developed to measure the viscoelastic properties of gelled hydrocarbons. In one form the instrument consists of a sphere which performs forced sinusoidal oscillations in the liquid to be investigated. The driving force is recorded as a function of amplitude and frequency. To evaluate the force on the sphere due to the viscous drag of the fluid, wall-, end-, and depth-effects as well as the nature of the surface of the sphere were studied. It was found that the observed force is particularly sensitive to the geometry of the instrument but relatively insensitive to the nature of the sphere. This work sheds light on the general applicability of existing sphere rheometers for the rheological characterization of non-Newtonian systems.

NAVAL WEAPONS CENTER
CHINA LAKE, CALIFORNIA * DECEMBER 1970

NAVAL WEAPONS CENTER
AN ACTIVITY OF THE NAVAL MATERIAL COMMAND

W. J. Moran, RADM, USN .... Commander

H. G. Wilson .... Technical Director

FOREWORD

A program at the Naval Weapons Center has been directed toward understanding the basic nature of gels and gelling processes. This report presents the results of the first phase of this program. The information, conclusions, and recommendations are developed with the hope of stimulating further research in this area.

This study was made in the period October 1968 to March 1969 under AIRTASK No. A31310/216/69R0010602 issued by the Naval Air Systems Command.

Because of the continuing nature of this work, refinements and modifications may later be made in the method and the measurements discussed.

This report was presented at the Winter Meeting of the Society of Rheology which was held in Pasadena, California on 2-4 February 1970.

Released by
WILLIAM S. McEWAN, Head
Chemistry Division
3 November 1970

Under authority of
HUGH W. HUNTER, Head
Research Department

NWC Technical Publication 5061

Published by.. Research Department
Collation............Cover, 7 leaves, DD Form 1473, abstract cards
First printing..................................180 numbered copies
Security classification.............................UNCLASSIFIED

CONTENTS

INTRODUCTION

The rheological behavior of simple Newtonian and complex non-Newtonian materials under isothermal conditions is usually determined by measuring the shearing stress as a function of the rate of shear. The results can be expressed in the form of a flow curve by plotting the rate of shear against the shearing stress. A Newtonian body is thus represented by a straight line for which the apparent viscosity coefficient in shear is constant. For other cohesive bodies such as gels the flow curves are generally found to be concave upwards, indicating pseudoplastic flow. At sufficiently high shear stresses in laminar flow the slope of the flow curve becomes constant and the body approaches Newtonian flow behavior with a limiting viscosity determined by the concentration and nature of the dispersed phase. If the fluid exhibits a yield value it can generally be determined by extrapolating either the upper, linear portion or, less reliably, the lower, curved portion of the flow curve to zero rate of shear.

The non-Newtonian flow behavior of viscoelastic bodies has been observed using a wide variety of highly developed, dynamic instruments. These include capillary, coaxial cylinder, telescopic shear, sliding parallel-plate, and cone and plate viscometers. More recently the rising sphere rheometer, originally conceived by McVean and Mattocks (Ref. 1), has been extensively used to measure the yield stress of gelled systems. With this instrument the force required to raise a sphere of known diameter at a constant, low velocity through the test material is measured. If it is assumed that a stress is applied to the gel from the entire surface area of the sphere, a yield value can be calculated by dividing the measured force corrected for buoyancy by the surface area of the sphere.

All of these instruments suffer from the theoretical objection that rheological information about the test material is obtained after the gel structure has been destroyed under various shearing conditions. Furthermore, since yield stress is a static property of a gelled system, it can be argued that data obtained under steady shear should not be extrapolated to static conditions. Nevertheless, a large body of practical and useful rheological information can be obtained with these instruments provided that their theoretical and experimental limitations are kept in the proper perspective.

The rheological examination of a viscoelastic substance such as a hydrocarbon gel is best carried out at very small shear strains. Effects due to thixotropic breakdown are eliminated and the sample may be considered to be in a nearly undisturbed state. Since measurements based on forced, sinusoidal deformations can be particularly valuable, a forced vibration rheometer was investigated.

The instrument was designed to cover the range of frequencies from 0.01 to 1.0 Hz, a range suitable for viscoelastic measurements since materials with fairly short relaxation times can be studied. The sinusoidal variations in force on a sphere at various input amplitudes and frequencies are displayed as Lissajous figures on a recorder or oscilloscope. Through an appropriate graphical technique (Ref. 2,3), the stress contributions of the viscous and elastic elements as well as the phase angle, the difference between the input sinusoidal strain and the resulting sinusoidal stress, can be evaluated. A simplified version of this apparatus has been described (Ref. 4).

It should be noted that sinusoidal deformations of a viscoelastic body by a sphere result in an extremely complex loading pattern. For example, since both normal and shear stresses are imposed on the body by the surface of the sphere the shear state cannot be rigorously defined (Ref. 5). This and other considerations led to the abandonment of sphere geometry in the forced vibration rheometer. However, many of the observations are directly applicable to the measurement of yield stress with a rising sphere rheometer. In this report, certain experimental results are described. Recommendations for improving the reliability and reproducibility of measurements of yield stress with a rising sphere rheometer are made.

EXPERIMENTAL

FORCED VIBRATION RHEOMETER

A schematic diagram of the complete apparatus is shown in Fig. 1. The gel specimen is strained by either a 1.91 or 2.54 cm solid Nylon or Teflon sphere suspended on a 0.0635 cm diameter rigid tungsten rod. Sinusoidal elongations having any amplitude in the range 0 to 0.75 cm were impressed upon the sample by a variable eccentric device. The latter was driven by a 600 rpm Insco Gearmotor (Cat. N18R0003) coupled to an Insco Model 00140 Step-Function Speed Reducer. Seven steps of the speed reducer were utilized to obtain output frequencies of 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, and 1.0 Hz.

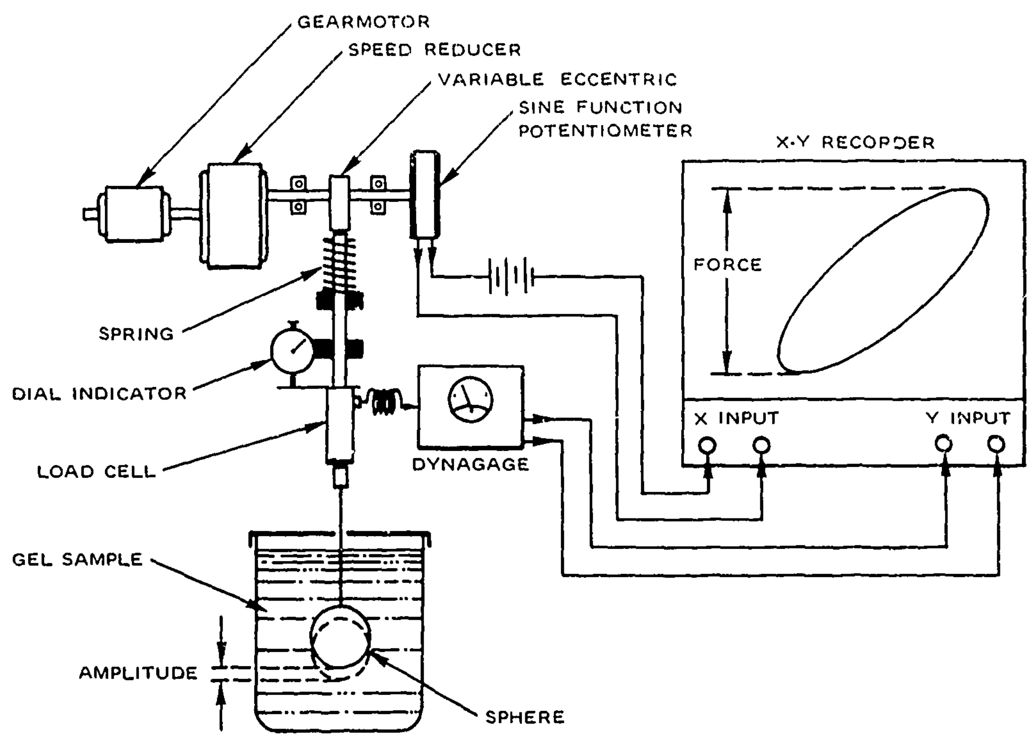

FIG. 1. Schematic Sketch of the Forced Vibration Rheometer.

Low range dynamic force ($\Delta F'$) on the sphere was measured with a Photocon Research Products Model 907 Load Cell (0-1 lb) in conjunction with a Model DG-600 Dynagage and a Model PS-600 Regulated Power Supply. A tenfold increase in sensitivity was obtained by attaching a simple lever mechanism to the diaphragm of the load cell. The output from the load cell was fed into the Y input circuit of an F. L. Moseley Co. Model 2D-2 X-Y Recorder.

Strain amplitude was initially set into the instrument with a dial indicator and then continuously monitored with a Beckman Instrument, Inc. Model NL5713 R20K C.5 Sin/Cos Potentiometer which was coupled to an extension of the output shaft of the speed reducer. The output from the potentiometer was fed into the X input circuit of the recorder.

All measurements were made at 24 ± 1°C.

SOLVENT

Baker and Adamson Reagent Xylene, comprising 9.3 wt. % o-xylene, 57.5 wt. % m-xylene, 14.4 wt. % p-xylene, and 18.8 wt. % ethylbenzene, was used.

GELLING AGENTS AND GELS

Shell AlMB2 Gellant--a proprietary material manufactured by Shell Development Co., Emeryville, Calif. A thixotropic gel containing 1.25 wt. % AlMB2 was prepared by high shear mixing in a Waring Blendor at ambient temperature.

Incendiary Oil Thickener M4--the diacid aluminum soap of iso-octanoic acid, containing principally dimethylhexanoic, methylheptanoic, and methylethylpentanoic acids. A 3 wt. % gel was prepared by prolonged, low shear mixing in a container turned on a set of rolls.

RESULTS AND DISCUSSION

EFFECT OF SPHERE SURFACE

The determination of yield stress using the rising sphere rheometer has been discussed in some detail in the literature (Ref. 1, 6, 7, 8, 9). All of these investigators have used a so-called "standard" steel or stainless steel sphere. However, Bost, et al. (Ref. 6) have given data for water gels from which it can be inferred that the material from which the shearing surface is formed has no influence on the measured stress. Capener and Tschoegl (Ref. 7), on the other hand, working with metal-loaded hydrazine gels, explicitly demonstrated that the surface has a profound effect on the measurement of yield strength with a rising plate and a parallel sliding-plate viscometer. Gold, chromium, aluminum, stainless steel, and Lucite surfaces were studied. The low yield values obtained with gold surfaces were attributed to adhesive failure on the surface.

In a limited series of experiments with the forced vibration rheometer it was found that the measured force was independent of the nature of the shearing surface. In Fig. 2, values obtained with 2.54 cm Nylon and Teflon spheres in an AlMB2-xylene gel are compared. While there is some scatter of the experimental points, it is quite clear that virtually identical results are obtained with these diverse surfaces.

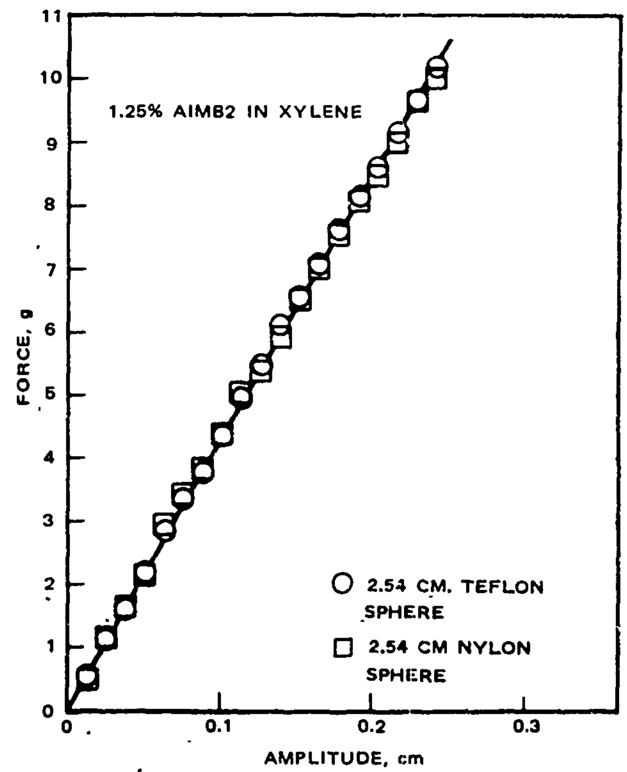

FIG. 2. Effect of Sphere Surface on Force Measurements. Frequency: 0.2 Hz.

It should be pointed out that the measured quantity may depend not only on the nature of the surface and its concomitant adhesive bond but also on the cohesive strength of the gel structure (Ref. 10). The latter is primarily dependent upon the nature and concentration of the dispersed phase, the type of solvent, the method and duration of mixing, the nature and amount of other materials added, and the previous stress history. Some of the poor reproducibility of measurements made with the rising sphere rheometer may be attributed to cohesive failure of the gel. Since definite information on the adhesive and cohesive strength of viscoelastic gels is not available at the present stage, it is difficult to discuss these features in more detail. More refined measurements should be made to clarify this problem.

EFFECT OF SPHERE DEPTH

In taking data with the rising sphere rheometer the sphere is initially positioned in the lower one-third of the sample at least one sphere diameter from the bottom of the sample container. In general, the height of sample above the sphere is not defined. Corrections for errors in the data due to the height of gel above the sphere have not been made by other workers.

Oscillatory measurements were made with the forced vibration rheometer by subjecting an M4-xylene gel to a sinusoidal strain of varying amplitude at a frequency of 0.2 Hz in a series of cylindrical containers. The force on a 2.54 cm Teflon sphere was measured in increments of one-half sphere depth starting at a point one-half sphere diameter below the surface of the gel.

Values of force are plotted versus amplitude in Fig. 3 for a 10.42 cm container. The data clearly show that the apparent viscoelastic resistance of the gel structure to the applied strain increases as the height of gel above the sphere increases. The set of data represented by the upper curve in Fig. 3 was taken with the sphere positioned about 0.5 cm above the bottom of the container and demonstrates the drag due to the stress on the bottom surface of the cylinder. Similar results were obtained in other containers.

An absolute correction for this effect would depend upon more detailed information about the complex dynamic shear modulus $G^*(\omega)$ of the particular gel being studied. The implication is, then, that to obtain more accurate and reproducible values of yield stress by the rising sphere method, it is essential to define the exact location of the sphere.

EFFECT OF WALL

A number of theoretical and empirical equations have been developed to correct for the influence of a solid wall on the motion of bodies in fluids. In the case of spherical symmetry the Faxén equation (Ref. 11) in the form

$$F = F_{obs}[1 - 2.104\ d/D + 2.09\ (d/D)^3 - 0.95\ (d/D)^5]$$

can be used to correct for the wall-effect when $d/D < 0.32$. In the above expression

F_{obs} = force reading of the load cell,

d = diameter of sphere,

D = diameter of container.

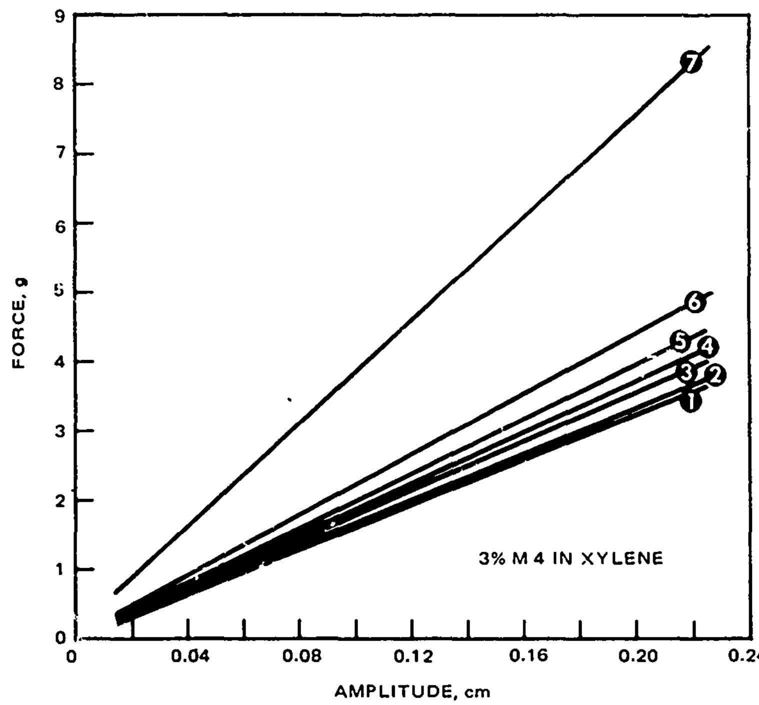

FIG. 3. Effect of Sphere Depth in 10.42 cm Container. The numbers on the curves correspond to:

Number	Depth in sphere diameters
1	0.5
2	1.0
3	1.5
4	2.0
5	2.5
6	3.0
7	0.5 cm above bottom

Only a few investigators have applied the Faxén correction to force measurements taken with the rising sphere rheometer (Ref. 1,7). However, Bost, et al. (Ref. 6) demonstrated a negligible wall-effect in containers of diameter greater than approximately 3.5 times the sphere diameter.

To examine the influence of the wall on force measurements taken with the forced vibration rheometer, experiments were carried out using d/D ratios which varied between 0.21 and 0.47. The family of curves shown in Fig. 3 is typical of the data obtained for an M4-xylene gel at 0.2 Hz in one container. Figure 4 shows uncorrected force values observed in all containers at a depth of one sphere diameter while Fig. 5 shows the same data after applying the Faxén correction.

It is clearly seen that the Faxén correction provides an adequate way to correlate data taken in large-diameter containers. Its use in the rising sphere technique is strongly recommended.

EFFECT OF FREQUENCY

As described previously, the forced vibration rheometer imparts small deformations to a sample so that the effect of varying amplitude and frequency can be measured. Assuming that Stokes' equation applies

$$F = 3\pi\mu VD$$

where F is the measured force, D is the diameter of the sphere, μ is the dynamic viscosity, and V is the average velocity of the sphere over one-half cycle rates of shear varying from 7.7×10^{-5} to 4.5×10^{-1} sec^{-1} are obtained for a 2.54 cm sphere.

As usually constructed a rising sphere rheometer provides rates of shear which vary between 2×10^{-4} and 8.5×10^{-1} sec^{-1}. Bost, et al. (Ref. 6,12) found that yield stress measurements are independent of the rate of shear. However, Capener and Tschoegl (Ref. 7) and Garmon, et al. (Ref. 13) have reported a dependence of stress on the rate of shear in the region around 10^{-3} sec^{-1}. The flow curve was extrapolated to zero shear and the intercept was taken as the yield stress. A similar technique has been used by Kirsch (Ref. 14).

A limited series of measurements made at various frequencies with the forced vibration rheometer is shown in Fig. 6. Here it is seen that, for an AlMB2-xylene gel, there was a moderate dependence of force on frequency, hence, rate of shear. Since the response of gels is obviously complicated by their composition and other factors, it is suggested that the relationship between rate of shear and shearing stress be examined in measurements made with the rising sphere rheometer.

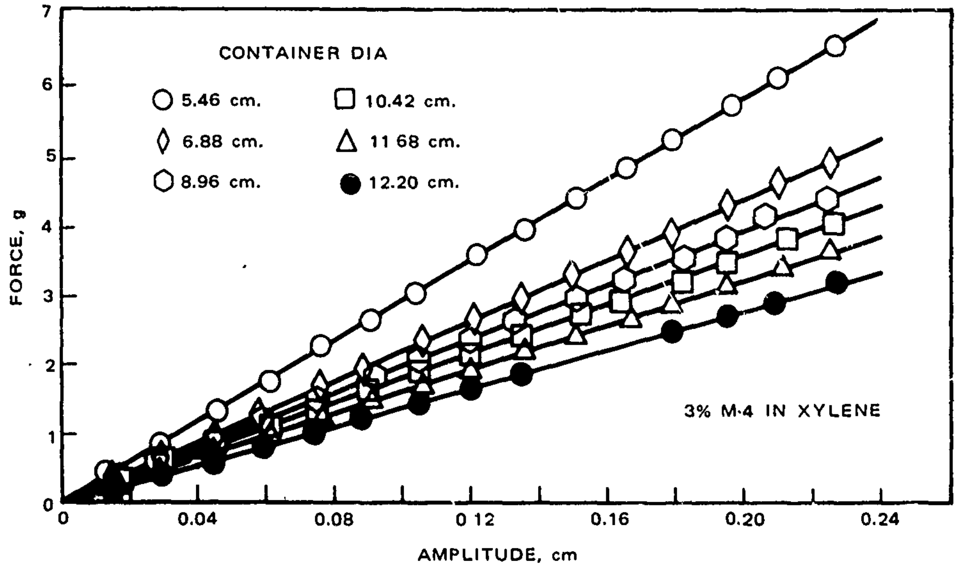

FIG. 4. Effect of Wall on Force Measurements Made With Sphere at Depth of One Sphere Diameter. Frequency: 0.2 Hz.

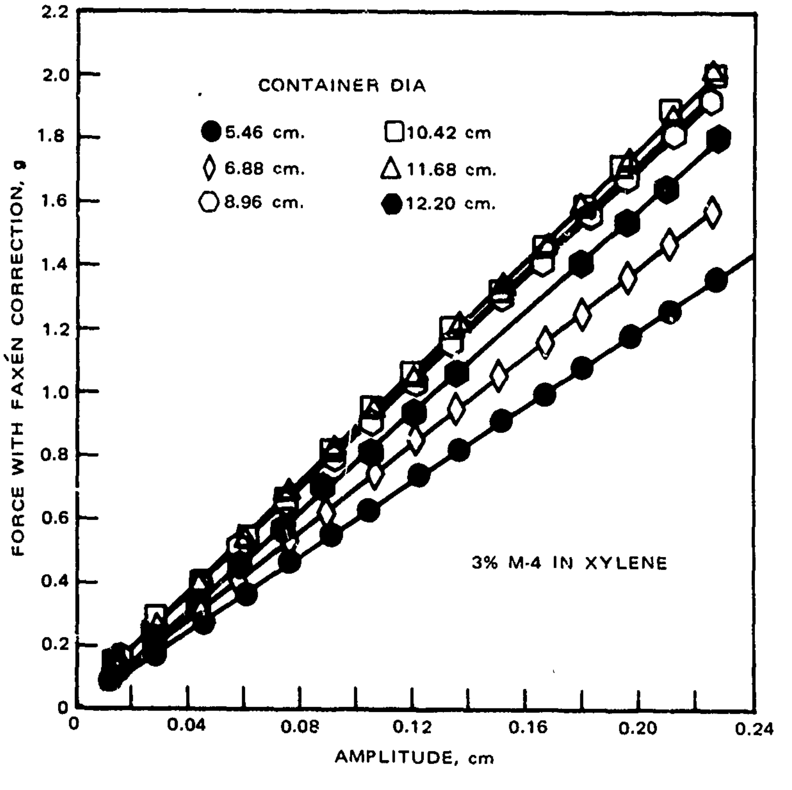

FIG. 5. Force Measurements of Figure 4 With Faxén Correction.

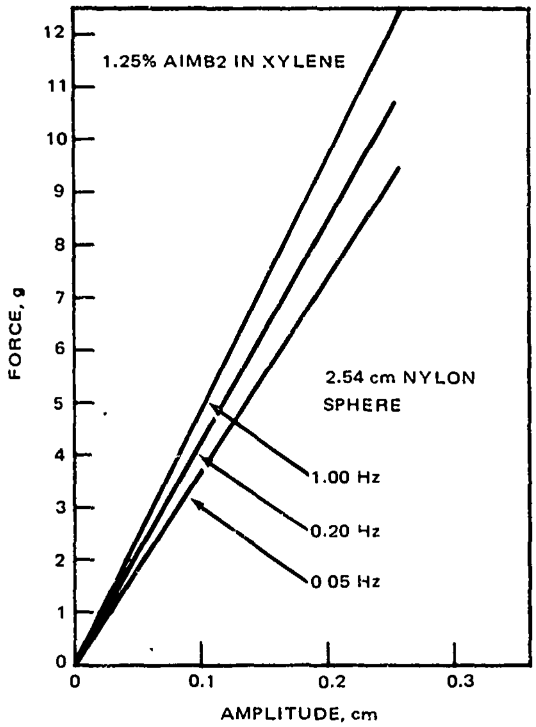

FIG. 6. Effect of Frequency on Force Measurements.

REFERENCES

1. McVean, E. E., and A. M. Mattocks. "Simple Rheometer for Definition of Viscoelastic Properties of Structural Liquids," J PHARM SCI, Vol. 50 (September 1961), pp. 785-88.

2. Van Wazer, J. R., J. W. Lyons, K. Y. Kim, and R. E. Colwell. Viscosity and Flow Measurement--A Laboratory Handbook of Rheology. New York, Interscience, 1963. Chap. 6, "Viscoelasticity and Its Measurement," pp. 329-89.

3. Bishop, R. E. D., and D. C. Johnson. The Mechanics of Vibration. Cambridge, Great Britain, University Press, 1960. Chap. 9, "Hysteretic Damping," pp. 449-93.

4. Tarsey, A. R. "Methods for the Rheological Characterization of Heterogeneous-Gelled Propellants," (U), presented at the 2nd Metallized Gelled Propellants Conference, AFRPL, Edwards, Calif., 26-28 August 1964. Publication CONFIDENTIAL.

5. Koshar, M., G. E. Mason, D. W. Brees, and P. S. Gakle. "Chemical and Physical Properties of Alumizine," (U), presented at the 2nd Metallized Gelled Propellants Conference, AFRPL, Edwards, Calif., 26-28 August 1964. Publication CONFIDENTIAL.

6. Aerojet-General Corporation. The Application of Yield Stress to Metallized Propellants, by J. J. Bost, P. S. Gakle, and C. B. DeSavigny. Sacramento, Calif., Aerojet, June 1963. (Chemistry Report No. R-038, Dept. 9221).

7. Capener, E. L., and N. W. Tschoegl. "The Measurement of the Yield Stress of Gel Structures," (U), presented at the 2nd Metallized Gelled Propellants Conference, AFRPL, Edwards, Calif., 26-28 August 1964. Publication CONFIDENTIAL.

8. U. S. Army Missile Command. An Investigation of the Rheology of Gels, by J. H. Blatt and B. D. Allan. Redstone Arsenal, Ala., USAMC, August 1966. (Report No. RK-TR-66-15).

9. MIL-P-27412 (USAF). Rising Sphere.

10. Air Force Rocket Propulsion Laboratory. Formulation and Evaluation of Liquid Propellant Dispersions (U), by Lionel A. Dickinson and Erwin L. Capener, Stanford Research Institute. Edwards, Calif., AFRPL, July 16, 1965. 30 pp. (AFRPL-TR-65-94, publication CONFIDENTIAL.)

11. Bacon, L. R. "Measurement of Absolute Viscosity by the Falling Sphere Method," J FRANKLIN INST, Vol. 221 (February 1936), pp. 251-73.

12. Bost, J. J., W. R. Fish, and P. D. Beadle. "Rheology of Gelled Metalized Propellants," (U), presented at the 2nd Metalized Gelled Propellants Conference, AFRPL, Edwards, Calif., 26-28 August 1964. Publication CONFIDENTIAL.

13. Garmon, R. C., D. H. York, E. H. Rowe, C. P. Talley, and J. E. Tessieri. "Aluminum-Loaded Hydrazine Gelled Propellant," (U) presented at the Metallized Gelled Propellants Conference, AFRPL, Edwards, Calif., 10-12 June 1963. Publication CONFIDENTIAL.

14. M. Kirsch, Rocketdyne, private communication.

UNCLASSIFIED
Security Classification

DOCUMENT CONTROL DATA - R & D

Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified

1 ORIGINATING ACTIVITY *(Corporate author)*

Naval Weapons Center
China Lake, California 93555

2a. REPORT SECURITY CLASSIFICATION

UNCLASSIFIED

2b GROUP

3 REPORT TITLE

Factors Influencing the Measurement of the Yield Stress of Gels With A Sphere Rheometer

4 DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Summary report

5 AUTHOR(S) *(First name, middle initial, last name)*

Warren J. Murbach, Arnold Adicoff, Alan L. Woodman, Albert H. Lepie

6 REPORT DATE	7a. TOTAL NO OF PAGES	7b NO OF REFS
December 1970	12	14

8a CONTRACT OR GRANT NO

b. PROJECT NO

AIRTASK A31310/216/69R0010602

c

d

9a. ORIGINATOR'S REPORT NUMBER(S)

NWC TP 5061

9b OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*

10 DISTRIBUTION STATEMENT

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Naval Weapons Center.

11 SUPPLEMENTARY NOTES

12 SPONSORING MILITARY ACTIVITY

Naval Air Systems Command
Naval Material Command
Washington D.C. 20360

13 ABSTRACT

A forced vibration rheometer was developed to measure the viscoelastic properties of gelled hydrocarbons. In one form the instrument consists of a sphere which performs forced sinusoidal oscillations in the liquid to be investigated. The driving force is recorded as a function of amplitude and frequency. To evaluate the force on the sphere due to the viscous drag of the fluid, wall-, end-, and depth-effects as well as the nature of the surface of the sphere were studied. It was found that the observed force is particularly sensitive to the geometry of the instrument but relatively insensitive to the nature of the sphere. This work sheds light on the general applicability of existing sphere rheometers for the rheological characterization of non-Newtonian systems.

UNCLASSIFIED

Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Forced vibration rheometer						
Rheology of gels						
Viscoelasticity						
Aluminum soap - hydrocarbon gels						
Shear rate						
Shear stress						
Viscosity						

DD FORM 1 NOV 65 1473 (BACK)

(PAGE 2)

Security Classification