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PERMEABILITY AND ADDITIVE SORPTION AND EXTRACTION IN LUBRICATING GREASES

BY

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ABSTRACT

The effect of the area and type of surface of ten silica thickeners and aluminum oxide on grease permeability, on the sorption of PAN[#] by the grease, and on subsequent extraction were studied.

For grease containing 6 % per cent of thickener, permeability coefficients varied from 20.1 x 10^{-11} cm^2 to 168 x 10^{-11} cm^2. For each silica type they decreased with increase in surface area of the thickener. The level of the permeability coefficient is generally related to the worked penetration.

In sorption measurements using permeating oils of varying PAN concentration, the amount of PAN associated with the thickener surface increased with PAN concentration. PAN concentration after equilibrium was reached was independent of the thickness of the grease cake. For each type of the silica thickener studied, the equilibrium PAN concentration increased with thickener surface area.

Extraction experiments were performed with oil containing no additive on the same grease samples on which sorption experiments were run. The final PAN concentrations were small. The differences among the final equilibrium concentrations of additive in the greases were a function of the type of silica thickener. No significant surface area trend was observed.

[#] **Phenyl-α-naphthylamine**

Initial rate constants for the additive exchange were the same for both sorption and extraction suggesting that the rate limiting step for replacement of the oil in the grease or for additive transfer between permeating oil and the oil in the grease is the same for the sorption and extraction experiments.

I. INTRODUCTION

A lubricating grease can be defined as " a solid or semifluid lubricant consisting of a thickening agent in a liquid lubricant. Other ingredients imparting special properties may be included " (1).

Many mechanical devices are constructed in such a manner that they can not be conveniently or efficiently lubricated by a liquid oil, but require a semisolid lubricating grease. The usefulness of lubricating greases in lubrication depends largely on the fact that the force per unit area necessary to produce continuous flow is not proportional to the rate of shear. This is known as non-Newtonian behavior (2). Since apparent viscosity is high at low shear rates, leakage from bearing is low compared with oils. In some applications, part of the grease acts as a seal to prevent leakage.

Greases are generally very complex owing to the fact that they are formed from thickener particles which are rarely pure chemical materials and usually mixtures of many chemical entities. These thickeners are then combined with oils containing many different types of molecules. Consequently, there are many interacting systems which make difficult any clear understanding of the fundamental nature of the thickener systems.

In recent years, the need for specialized lubricants has increased because of the use of higher precision, heavily loaded and more specialized machinery. At the same time, the lubricating grease industry has made notable progress in transforming grease making from an art to a science. Sodium, barium, lithium and calcium complex soap thickeners have been used in recent years along with synthetic fluids such as polyglycols, phosphate esters, dibasic esters, silicone and polyphenyl esters etc (3).

Nevertheless, there is still a great deal of uncertainty about the fundamental properties and the mechanical behavior of lubricating greases. Very little exact information is available on the relations between composition and structure of greases.

Several years ago Sisko and Brunstrum suggested the use of permeability measurements as a means of deducing information about the structure of a lubricating grease. Tu (4) and Lin (5) have made permeability measurements to investigate the effect of mineral oil type and viscosity on thickener structure. Part of this study is an extension of their work. The effect of the area and type of surface of various silicas on grease permeability was examined holding mineral oil and manufacturing procedures constant.

Additives are substances added to lubricating greases to obtain or enhance properties desired in the final product. Some additives have been known and used for many years, but the mechanisms of additive action are not understood. Additives of low concentration are widely used in lubricating greases for oxidation inhibition, rust protection, load carrying enhancement, etc. Some additives with concentrations as low as 0.1 % affect the mechanical stability and presumably the structure of a grease while others with much higher concentrations have little effect.

If we were able to understand more fully the mechanism of additive action in lubricating greases and the effect of additive concentration on the improvement of particular properties, then we would be in a better position to control the formation of desirable greases during manufacture and to improve the particular properties of the special greases.

As a first step in studying additive effects, Zakin, Tu and Lin (6) have made exploratory studies of the sorption and extraction of additives (PAN) on a lithium hydroxystearate grease and on a modified clay thickener grease. Another part of this investigation was to study the sorption and extraction results on a series of greases containing different kinds of silica thickeners.

II. LITERATURE REVIEW

A. Grease Permeability

Permeability is the measurement of the ease with which a fluid of a given viscosity flows through a solid mass. Therefore, permeability measurements provide some information on the nature of the grease structure, and on the "tightness" with which the thickener holds the oil.

Greases generally bleed oil slowly in storage, in pumping, and in service. In many applications the bearing operates at a relatively low temperature, and a grease which will supply an adequate amount of oil under these conditions will naturally bleed in storage. The amount of oil that is lost under normal conditions is trivial in relation to the quantity still contained in the grease, and the qualities of the grease as a lubricant will be unaffected. The tendency to separate oil is determined by a number of factors such as the nature of thickener and the oil, the composition of the thickener, time, pressure and the nature of the service. Several authors (7, 8,9) predicted that the most important factor affecting the oil separation was the nature of the grease structure. Baker (10) claimed that a good grease should possess the property of low initial rate of oil separation, but should have the property of being able to give up a high proportion of its oil for long ball bearing life.

In 1960 Sisko and Brunstrum (11) suggested that a lubricating grease could be considered as a permeable mass and that flow of fluid through the lubricating grease would obey Darcy's law. Darcy's law (12) of permeability states that the rate of flow is directly proportional to the pressure gradient causing flow

$$u = - B_1 \frac{\partial P}{\partial x} = B_1 \frac{\Delta P}{L} \text{ ------------------ } (1)$$

where $\frac{\partial P}{\partial x}$ is the pressure gradient, Δp is the total pressure drop across a sample of length L, and B_1 is a permeability coefficient. Because permeability is determined by the size, shape, concentration and dispersion of particles in the thickener network, they suggested the use of permeability measurements to study the structure of the network, oil separation from grease, and uniformity of particle dispersion througnout the grease.

For this purpose they designed an apparatus which is shown in Figure 1. Permeabilities are determined by allowing the oil to flow through the grease under its own head. The change in oil height is measured as a function of time. Assuming the density of the oil to be constant, the velocity of flow, according to the law of continuity, is

$$u = - \frac{R_2^2}{R_1^2} \frac{dh}{dt} \text{ ------------------ } (2)$$

where R_1 = radius of the sample

R_2 = radius of the pipette connected with the adaptor

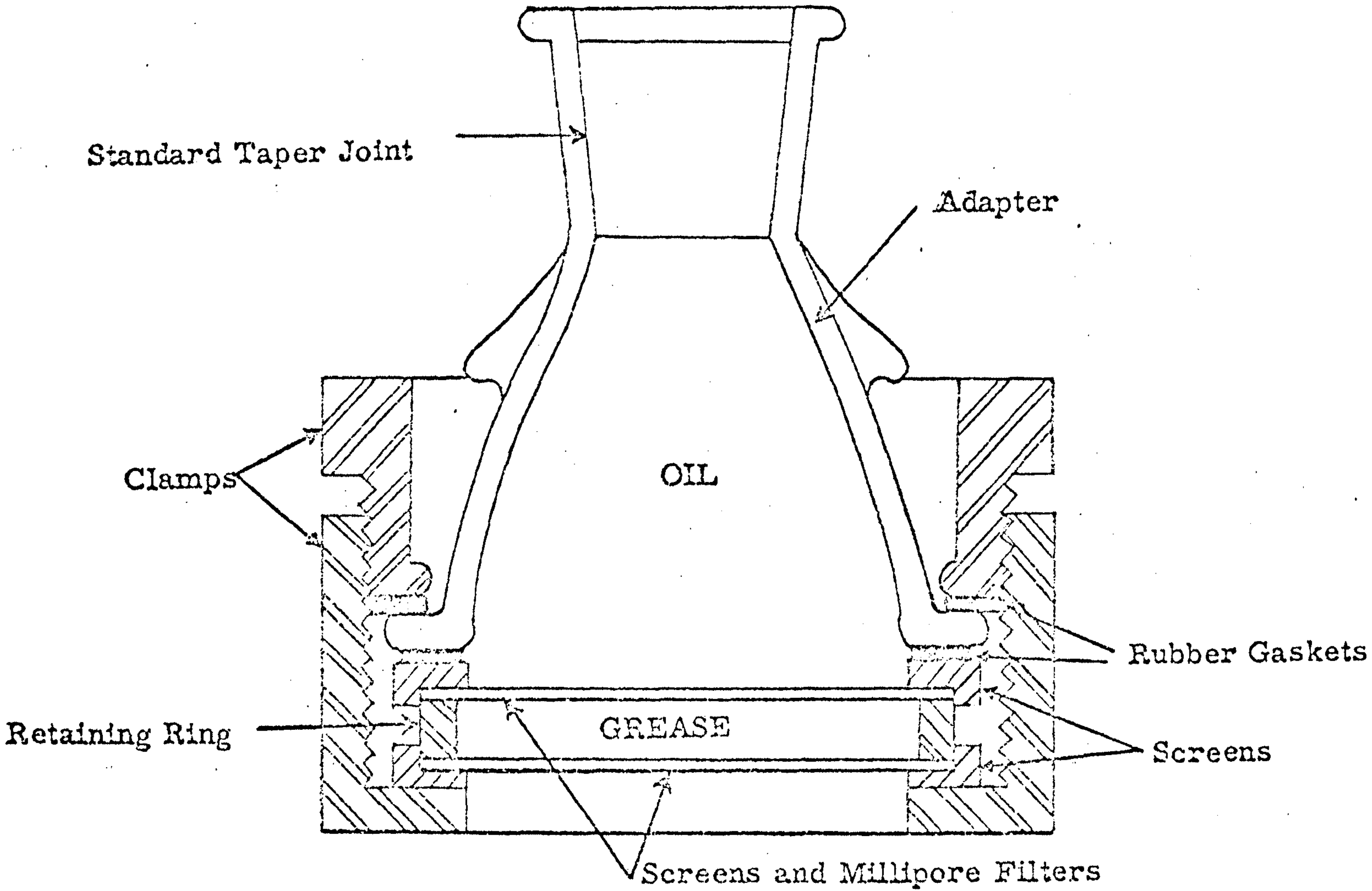

Figure 1. Permeability Apparatus Diagram

and h = height at time t

For the measurement of grease permeability, the flow direction is vertical, the bed is horizontal and laminar flow prevails. This condition implies (1) that resistance to flow is entirely due to viscous drag and (2) that the fluid is inert to the porous medium, i,e, chemical, adsorptive, electrical, electrochemical and capillary effects are absent. We can then add that the rate of flow is inversely proportional to viscosity and introduce another specific permeability coefficient, B_o, for viscous flow.

$$u = V_s = -\frac{B_o}{\eta}\frac{\partial P}{\partial X} = \frac{B_o}{\eta}\frac{\Delta P}{L} \text{ ------------------- } (3)$$

where

V_s = effluent rate per unit cross-sectional area, cm per sec.

P = pressure drop across the sample, dynes per cm^2

L = thickness of the sample, cm

η = viscosity of the oil, poise

B_o = specific permeability coefficient, cm^2

The pressure drop across the sample is ρgh, where

ρ = density of the oil, in gm per cc

g = acceleration of gravity, in cm per sec^2.

h = height of the oil level, in cm

Substituting these values of u and ΔP into Equation (2) gives the working equation for calculating the permeability coefficient:

$$-\frac{R_2^2}{R_1^2}\frac{dh}{dt} = \frac{B_o \rho gh}{\eta L} \text{ ------------- } (4)$$

where η/ρ is the kinematic viscosity, ν.

This equation can be written as:

$$B = - \frac{\nu L R_2^2}{g R_1^2} \cdot \frac{d \ln h}{dt}$$

$$= - K \frac{d \ln h}{dt} \text{ ------------ } (5)$$

where $K = \frac{\nu L R_2^2}{g R_1^2}$ which is constant for a particular oil and apparatus at constant temperature.

From Equation (5), plots of ln h vs. t are linear with negative slopes from which the permeability coefficient can be calculated.

Sisko and Brunstrum (11) observed that for a series of greases, oil separation using the ASTM test method and the ratio of permeability to viscosity were in the same order, but the relationship was not linear. They also noted that as the percent of worked rheopectic grease in a grease mixture increased, the permeability coefficient of the mixture decreased, indicating the effect of structure on permeability.

Ewbank and co-workers (13) demonstrated the validity of Darcy's equation for describing the permeability of lubricating greases. They also found that the permeability decreased with increase in the concentration of the thickener, the mathematical form of the relationship being logarithmic.

$$B = A e^{-kc} \text{ ---------- } (6)$$

where A = constant

K = constant, characterizing the nature of the thickener

C = weight per cent thickener in grease

Zakin and Tu (14) used greases thickened with lithium-calcium soaps and with Baragel to study the effect of viscosity and type of oil component on the permeability coefficient. They found that the permeability coefficients for greases made with these thickeners are dependent on the type and viscosity of the lubricating fluid from which the grease is made. Lithium-calcium and Baragel greases made with paraffinic oils had equal or higher permeability coefficients than greases made with naphthenic oils of the same viscosity at the testing temperature. With naphthenic oils, permeability increased with increase in viscosity in both the lithium-calcium and the Baragel greases. With paraffinic oils, the permeability coefficient was much less sensitive to oil viscosity for both thickeners.

Lin (5) studied the effect of variations in the viscosity and type of the mineral oil component on the permeability coefficient in greases thickened with Cab-O-Sil M-5 and Cab-O-Sil H-5. The permeability results showed no significant differences between the two thickeners, although H-5 has a surface area 62.5 per cent greater than M-5 and presumedly a smaller ultimate particle size. For both thickeners, the permeability of greases made with paraffinic oils gave higher values than those made with naphthenic oils of the same viscosity at 77° F. The effect of the viscosity of the oil component used in manufacture on the permeability coefficients was not large.

B. Nature of Adsorption and Surface Properties of Thickener

Surface tension may be defined as a free energy. The component having the lowest surface tension will be enriched in the surface layer as a result of the tendency of a system to have the minimum surface free energy. This enrichment of a component in the surface layer is called adsorption, and it occurs at all interfaces (15).

Molecules inside any solid are subjected to equal forces in all directions whereas those in the surface are subjected to unbalanced forces. If other molecules become attached to the surface, they can balance the resulting inward forces. The attractive forces are the same as those responsible for surface tension and condensation in liquids. They are relatively weak and are called Van der Waals' forces. The adsorption is regarded as "physical" and the adsorbed molecules are easily released from the surface when Van der Waals' forces are involved.

Presently, there is no known direct method to measure the surface tension of a solid. However, due to the fact that the total surface energy is equal to the product of the surface energy per unit area and the total surface area, high surface area is a major consideration in adsorption experiments.

C. Additives in Greases

There are many definitions of additives in grease. Webber (17) defined additives as "substances which impart or enhance the desirable properties of a lubricant and eliminate or minimize the deleterious ones". Thus, the function of the additive is to improve the properties of the lubricating grease hopefully without changing its structure to any extent. According to their functions, Boner (1) has classified the grease additives into ten categories, such as oxidation inhibitors, corrosion and rust inhibitors, etc.

From the experiments of Tu (4) and Lin (5) on extraction and adsorption of phenyl-α-naphthylamine (PAN), it was shown that the amount of additive sorbed by a modified clay-thickened (Baragel) grease at equilibrium was greater than that sorbed by lithium grease, although the initial rates of sorption were about the same. The amount of additive associated with the thickener appears to increase with increasing additive concentration from less than 0.002 gm per gm thickener in equilibrium with the 0.5 per cent PAN solution to 0.03 gm per gm of thickener in equilibrium with the 3 per cent PAN solution. The Baragel grease sorbed considerably more PAN, ranging from 0.07 gm per gm of thickener at a PAN concentration in the equilibrium oil of 0.5 per cent to 0.16 gm per gm of thickener at a PAN concentration of 3 per cent. Lin (5) extracted PAN from the two greases with additive free oil. This resulted in almost complete removal of PAN from the lithium grease, but about 0.2 per cent PAN was retained in the Baragel grease. Lin (5) also ran exploratory sorption and extraction experiments with silica grease but got anomalous results.

D. Infrared Analysis

Both Tu (4) and Lin (5) used infrared analysis to obtain the PAN concentration in the exit oil samples.

Infrared absorption spectra are characteristics of the functional groups in the sample and can be used to establish the presence or absence of certain groups. Most useful additives contain active functional groups. These groups can be used to identify qualitatively and quantitatively the specific chemical groups in a compound from their spectra. With unknown materials, an infrared curve may indicate the functional groups that are present.

By the application of a combination of two fundamental laws we can relate the magnitude of the infrared absorption with the amount of material causing it. The relationship between the amount of absorption and the thickness of the absorbing medium can be expressed by one of these laws, known as Lambert's (19) law. It states that the absorption of monochromatic radiant energy in passing through an optically homogeneous system is directly proportional to the length of the absorbing path.

The other law, postulated by Beer (20), expressed the relationship between the amount of absorption and the concentration of solute causing the adsorption. It states that the absorption of incident energy is directly proportional to the concentration of the absorbing entity.

In analytical applications it is customary to combine these two laws into an equation of the following form $\log P_o / P = A = a\ b\ c$, where P_o is the radiant energy incident on the sample, P is the radiant energy after passing through the sample, A is the absorbance, a is a constant called absorptivity, b is the cell thickness and c is the concentration.

Beer's (20) law predicts that the absorbance A is a linear function of the concentration of the absorbing material. However, deviations from Beer's law are to be expected whenever the slits are wider than the width of the absorption band used (21). If the slit widths are appreciably wider than the band widths, deviations will occur at low transmittances. So Robinson (21) suggested working at high transmittances.

III. EXPERIMENTAL

A. Preparation of Silica Grease

1. Raw Materials

a. Mineral Oils

A 500 sec. solvent refined naphthenic oil (oil J of Reference 5) obtained from the Mobil Oil Company was used in making all of the greases. The viscosity of the oil at 77°F is 219 CSTKS, with specifications of viscosity index 70, aniline point 213°F, and viscosity gravity constant 0.832.

b. Thickeners

The greases used in the experiments were prepared from the following silica thickeners and aluminum oxide. The chemical and physical properties of these thickeners are shown in Table I.

(1) CAB-O-SIL

Two grades of Cab-O-Sil thickener (H-5, M-5) obtained from the Cabot Co. were used. Cab-O-Sil is a submicroscopic pyrogenic silica prepared at high temperature (1100°C) by the vapor phase hydrolysis of silicon tetrachloride.

(2) AEROSIL

Four grades of Aerosil thickener (uncompressed, 2491, 2491-380, MOX-170) were obtained from Degussa Inc. Aerosils are submicroscopic pyrogenic silicas produced by flame hydrolysis of silicon tetrachloride in a

TABLE I

Chemical and Physical Properties of Silica and Aluminum Oxide Thickeners

Thickener	Cab-O-Sil H-5	Cab-O-Sil M-5	Aerosil Uncompressed	Aerosil 2491	Aerosil 2491-380	Aerosil Mox-170	QUSO G-32	QUSO F-22	Santocel C	Santocel Z	Aluminum Oxide
Silica Content	99.8	99.8	> 99.8	>99.8	>99.8	>98.3	98	98	92-94	90-92	0.1
Ultimate Particle Size (mμ)	0.007	0.012	0.01--0.04	0.005--0.02	0.003--0.015	0.01--0.03	0.013	0.012	0.01--0.02	0.01--0.02	0.005--0.03
Surface Area m^2/gm	325	200	200 ± 25	300±30	380±40	170±30	300	325	130	280	100±10
Bulk Density lbs/ft^3	2.3	2.3	2.5-3.5	2.5-3.5	2.5-3.5	2.5-3.5	4	4	6.7	3.3	-
Specific Gravity	2.2	2.2	-	-	-	-	2.1	2.1	-	-	-
p^H	3.9	4.0	3.6-4.3	3.6-4.3	3.6-4.3	1.45	8.5	5.0	3.8	4.0	4-5

gaseous environment at 1100°C.

(3) QUSO SILICA

Two grades of Quso Silica thickener (G-32, F-22) were obtained from the Philadelphia Quartz Company. Quso Silica is a micro fine precipitated silica.

(4) SANTOCEL SILICA

Two grades of Santocel Silica thickener (C, Z) were obtained from the Monsanto Company. Santocels are produced from a water solvent system under high pressure above the critical point of the water solvent phase. The structure of these materials would be termed micro porous in nature.

(5) ALUMINUM OXIDE

Aluminum Oxide thickener was obtained from Degussa Inc.

2. Manufacturing Procedure for Silica Greases

Solvent refined Naphthenic oil (940 g or 94 %) and silica thickener (60 g or 6 %) and 2 cc of water were mixed with a spatula in a five pound grease kettle. The mixture was then stirred with the double motion paddle stirrer with scraper blades for 60 minutes without heat. The thickened mix was then homogenized by passing through a Morehouse Mill three times. The clearance between the upper stationary mill stone and the lower high speed rotor stone was adjucted to 0.001 inches.

B. Permeability Measurements

1. Permeability Apparatus

Figure 1 shows the apparatus designed by Sisko and Brunstrum (11) for the measurement of permeability. The apparatus consists of a 5 cc pipette with a wide opening at one end and a ground glass joint at the other end which is connected by a bell-shaped glass adaptor to the main sample assembly. The sample is retained inside a stainless steel ring about 0.5 cm high and 4.16 cm in diameter. A millipore filter paper (type HA*) is supported on a 40 mesh ring. The entire sample assembly is held within a pair of screw clamps. A neoprene gasket is placed on the extended base of the adaptor to ensure a tight fit for the entire assembly.

2. Permeability Measurement Procedure

a. Sample Packing Technique

In packing the grease samples, one of the most serious problems is the presence of air bubbles in the sample, since they affect the properties of the sample and may therefore cause serious error in the experimental results. Therefore a procedure was developed to minimize the amount of air in the sample. The grease sample was charged into a 10 cc medical syringe. The grease was then carefully discharged from the syringe into the sample retaining ring along the edge of the ring. A piece of drawn glass tubing connected to

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* Millipore Filter Corporation, Bedford, Mass.

an ordinary water aspirator was used to suck air bubbles out of the grease sample. This procedure of charging and sucking air was continued until the retainer was filled with grease containing no visible air bubbles. To make the sample surface flat and smooth, excess grease was then wiped off with a spatula.

b. Permeability Measurements

After cleaning the permeability apparatus, a piece of filter paper wetted with the same oil from which the grease was made was placed on the bottom screen, while the excess oil was removed with absorbent tissue. The retaining ring was then placed on the filter paper and grease was packed into it by the sample packing method described above. The top screen was then put in place. The sample assembly was placed in the bottom half of the clamp and in succession, a neoprene gasket, the bell-shaped adaptor, another gasket and the top half of the screw clamp were added. The clamps were then screwed together tightly by hand. The adaptor was filled with oil, and the pipette was mounted on the ground glass joint of the adaptor. A film of grease was put between the pipette and the ground glass joint of the adaptor. Two springs were attached to hold the pipette tightly in place to prevent the oil from leaking. The pipette was then filled with oil to the 5 ml. mark. The sample was then placed in a 400-ml beaker set on a plastic rack immersed in a constant temperature water bath at 77° F ± .05°F. The water level reached to the top of the adaptor.

After the pipette was filled with oil, measurements were delayed for a few hours to make sure any air bubbles trapped in the oil rose to the surface. A small amount of additional oil was added after all the air bubbles were removed and the initial height reading was taken. The oil height was read at periodic intervals depending on the oil flow rate. Runs were terminated after 10 to 80 hours or when the liquid level fell below the pipette scale. At least three runs per sample of grease were made. A typical run is shown in Figure 2. Permeability coefficients were calculated directly from the data using a least squares procedure to obtain the slope of logarithm of oil height versus time data. Sample calculations are given in Appendix A.

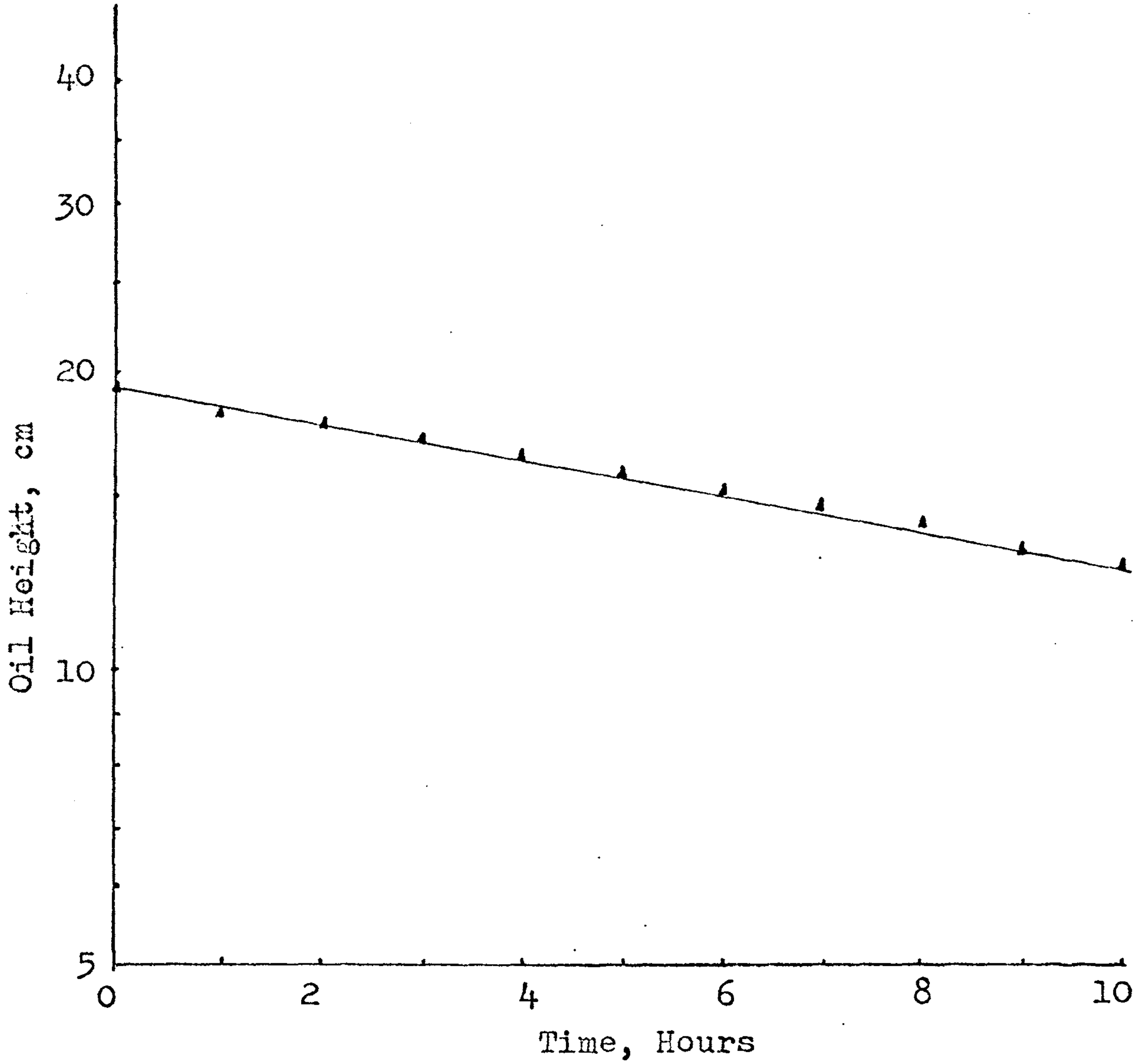


Figure 2 Oil Height vs. Time Data for Grease Containing 6 % Aerosil Uncompressed Silica Thickener.

TABLE II

Consistencies of Silica and Aluminum Grease

Thickener	Grease Consistency (penetration Test)		Bleeding Tendencies after Four Months' Storage
	Unworked	Worked	
Aerosil Uncompressed	298	304	No bleeding
Aerosil MOX-170	356	380	No bleeding
Aerosil 2491	256	270	No bleeding
Aerosil 2491-380	279	282	No bleeding
Aluminum Oxide	387	409	Slight bleeding
CAB-O-SIL H-5	278	284	No bleeding
CAB-O-SIL M-5	284	300	No bleeding
QUSO F-22	388	391	Bleeding only in pockets
QUSO G-32	378	387	Bleeding only in pockets
Santocel Z	296	301	No bleeding
Santocel C	401	408	Bleeding

C. Sorption and Extraction Measurements

Sorption experiments were run in which oils with 0.25 %, 0.5 %, 1 %, 2 %, and 3 % of PAN additive were permeated through silica grease samples without additives. After each sorption experiment reached equilibrium, an extraction experiment was run in which oils without additives were permeated through the same grease sample.

1. Sorption Measurements with a Range of Additive Concentrations

Using the sample packing method described in Section B, grease samples without additives were packed into the permeability apparatus sample retainer. The apparatus assembly was set up as usual. The pipette was filled to the 5 cc mark with oil containing a known per cent of additive. The apparatus was then placed on a 250 cc beaker at room temperature. Effluent samples were collected for IR analysis and oil heights were recorded. Oil sticking to the bottom of the apparatus was sucked up with a medicine dropper and added to the sample bottle together with the oil from the bottom of the beaker. To maintain the oil height, fresh oil was added to the pipette. Most oil samples had a volume of 1 to 2 cc of oil. These experiments were terminated when equilibrium was reached. That is, when the concentration of the additive in the exit oil was the same as that in the original oil permeating through the grease sample. It took from 3 to 20 days to reach equilibrium and the total amount of exit oil varied from

18 to 35 cc. The oil samples were analyzed with a Beckman IR-5A Model Spectrophotometer to determine the additive concentration in the effluent oil. Additive concentrations in the grease were computed from mass balances on the PAN. Three typical runs are shown in Figure 3.

2. Extraction Measurements after Sorption Experiments

After equilibrium was reached, the apparatus was disassembled and all parts except the grease retainer were cleaned thoroughly. The oil present on the outside of the filter was wiped off with a tissue. The grease retainer was then reassembled in the apparatus for the extraction experiment and the pipette was filled with oil without additive which was then permeated through the grease sample. The procedure then followed that in the sorption experiment. When the exit oil contained no additive, that is, when equilibrium was reached, the extraction experiment was terminated. The time required for reaching equilibrium varied from 3 to 20 days and the total amount of effluent oil varied from 18 to 40 cc.

3. Sorption and Extraction Measurements with Different Thickness of Grease Cake

Silica grease samples thickened with 6 % Cab-O-Sil H-5 silica thickener were packed into the permeability apparatus with ring thicknesses of one half and double the normal thickness. Sorption and extraction experiments were then run in the same manner as described in Sections 1 and 2.

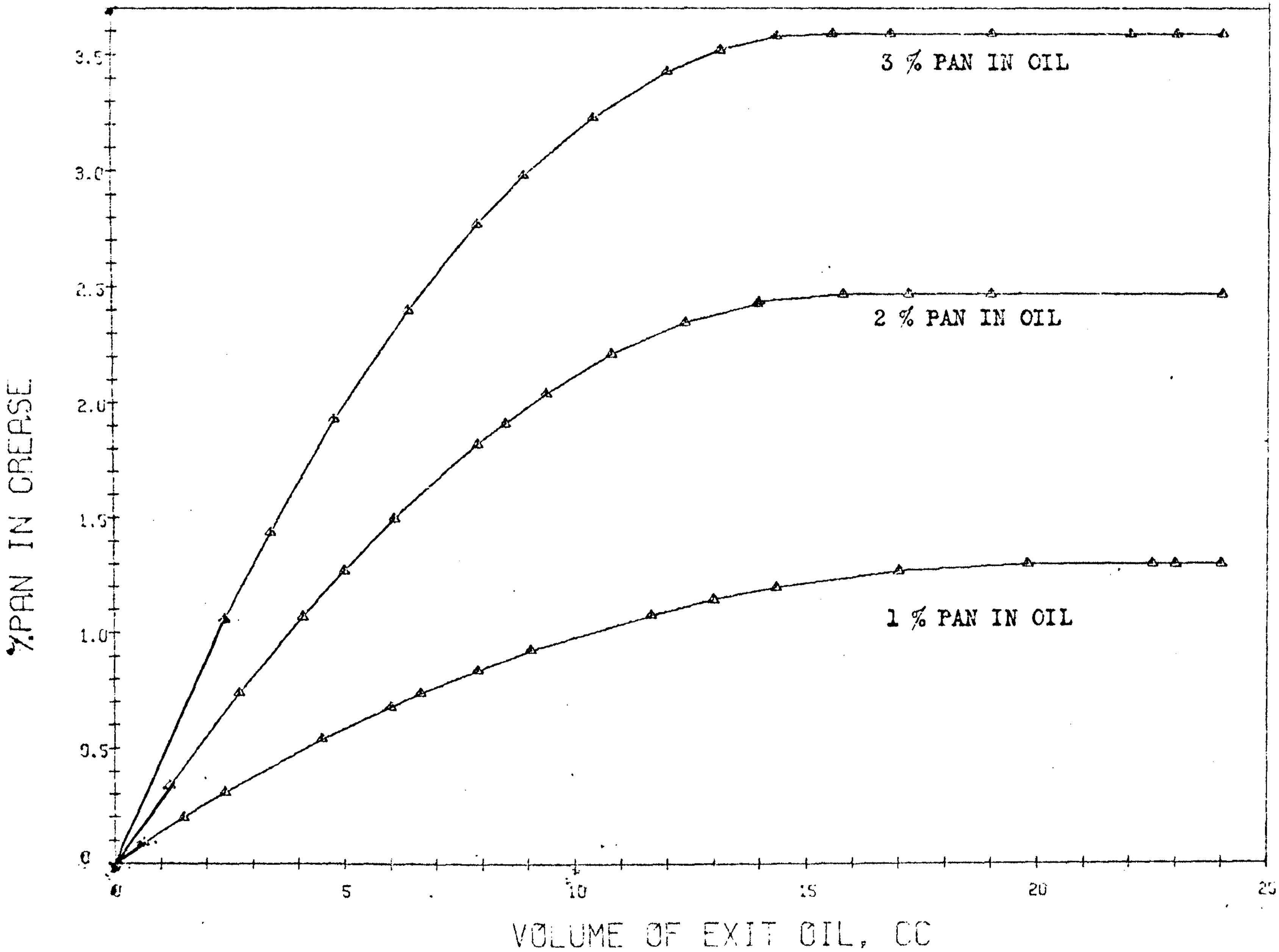


Figure 3 Effect of Volume of Permeating Oil on % PAN in Grease

D. Analysis for Additive

In order to determine the amount of additive picked up or lost in the sorption and extraction experiments, a simple but accurate analytical method was needed to measure small amounts of additive in the effluent oil. Both infrared and ultraviolet absorption spectra of lubricating oils with additives were considered.

Since the infrared absorption is due to interactions of the light waves with the vibrations of the atoms within a molecule, whereas the ultraviolet absorption is due to interaction with the very much lighter valence electrons, vicinal effects in infrared should be less important and should hardly extend beyond the second neighbor distance from a given bond. Sensitivity to vicinal effects is a major obstacle to the ultraviolet absorption spectrum analysis of lubricating oils (15). Infrared analysis provided a sensitive absorption band for the additive (PAN) at a wave number of 770^{-1}cm.

1. Description of Infrared Spectrophotometer

A Beckman Model IR-5A Spectrophotometer (16) was used for these measurements. It is an automatic recording, single-beam, double-beam instrument designed for the qualitative and quantitative chemical analysis of liquid, solid and gaseous phase samples and equipped with NaCl optics. Two NaCl crystals 0.2 mm apart form the slit which holds the film-type liquid sample. This pair of crystals is mounted on a brass frame to form the complete sample cell or reference cell. The IR-5A has a wave length range of 2 to 16 microns. The instrument records linearly in per cent transmittance and wave length.

2. Infrared Analysis Procedure

a. Selection of Additive and Band Peaks

Two common additives used in greases, phenyl-α-naphthylamine (PAN) and Paratertiary butyl catechol (Ionol), were examined for sensitivity to infrared detection at low concentrations in oil solutions.

The IR Spectra absorption curve for PAN had bands at 1570 cm^{-1}, 770 cm^{-1} and 1480 cm^{-1}. At high concentrations of PAN, there was also a band at 685 cm^{-1}. Relative heights of the absorption peaks for PAN and Ionol are shown in Table III and Table IV for differential analysis. The IR Spectra absorption curve for PAN had more sensitive absorption bands than that for Ionol. The peak at 770 cm^{-1} was chosen for analysis for two reasons: (1) the sensitivity of detection is greatest here because a maximum change in absorbance occurs here per unit concentration change, and (2) the absorbance change with concentration at this wavelength is more nearly constant over the concentration range of interest (up to 3.0 per cent) and therefore leads to maximum precision in the overall determination.

b. Details of Procedure

TABLE III

Height of PAN Absorbance in the Infrared Spectra

(One Unit = One Division on Chart = 0.05 Inches)

	Wave Number, cm^{-1}		
% PAN in Oil	770	1480	1570
0.1	2.9	-	2.0
0.2	6.6	1.0	3.1
0.3	9.8	2.1	4.3
0.4	15.1	2.8	7.6
0.5	18.5	3.2	10.0
0.6	21.5	5.1	12.5
0.7	24.7	6.2	14.8
0.8	28.5	7.1	17.7
0.9	32.4	8.0	19.8
1.0	35.0	10.1	20.8
1.5	44.3	12.5	28.5
2.0	52.2	14.5	35.8
2.5	59.3	17.5	39.1
3.0	63.2	20.6	41.5

TABLE IV

Height of Ionol Absorbance in the Infrared Spectra

(One Unit = One Division on Chart = 0.05 Inches)

	Wave Number, cm^{-1}		
% Ionol in Oil	860	1160	3700
0.10	0.9	1.1	1.0
0.25	2.0	2.1	2.2
0.50	3.5	3.6	4.2
1.00	10.0	8.1	8.5
2.00	21.0	19.0	16.5
3.0	31.0	28.0	22.5

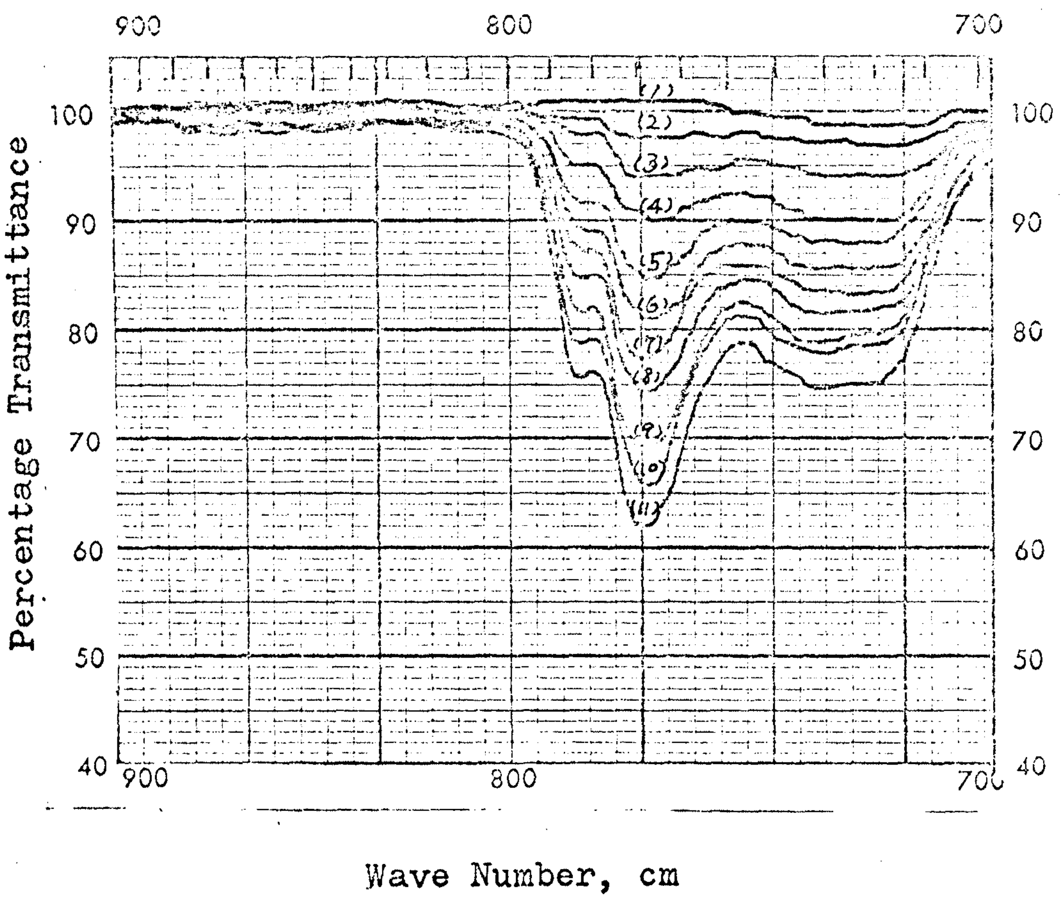
(1) Differential Quantitative Infrared Analysis

A technique known as differential infrared analysis is particularly useful when applied to lubricating oils with additives. In this technique, a sample of pure oil without additives is placed in the reference cell of a double beam infrared spectrophotometer and the oil with additives in a matched sample cell. Thus, the absorbance due to the oil itself is compensated, and the net absorbance is due to differences in chemical composition between the pure oil and the oil containing additive.

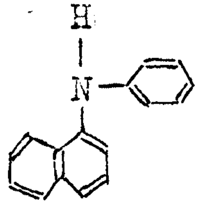
Calibrations were made using 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.5, 2.0, 2.5, 3.0 % PAN in oil J. The band peaks of PAN increased gradually as the concentration of additives in oil J increased (see Table III and Figure 4). From these data a calibration curve was drawn (see Figure 5).

(2) Experimental Procedure

The two NaCl crystal cells were cleaned thoroughly with volatile solvent (benzene) and dried with compressed air. Two drops of pure oil J were inserted into one of the openings of the reference cell with the help of a medicine dropper. A medical syringe filled with oil was then mounted over the end opening. By pushing the rod down gently the oil flowed down the narrow slit and formed a 0.2 mm thick oil film through which the infrared beam was projected. Air bubbles had to be prevented from getting into this film.



$C_{16}H_{13}N$



Phenyl-α-naphthylamine

(1) 0 % PAN in oil J (pure oil J)
(2) 0.1 % PAN in oil J
(3) 0.2 % PAN in oil J
(4) 0.3 % PAN in oil J
(5) 0.4 % PAN in oil J
(6) 0.5 % PAN in oil J
(7) 0.6 % PAN in oil J
(8) 0.7 % PAN in oil J
(9) 0.8 % PAN in oil J
(10) 0.9 % PAN in oil J
(11) 1.0 % PAN in oil J

Figure 4 Portion of a Double Beam Projected IR Spectra

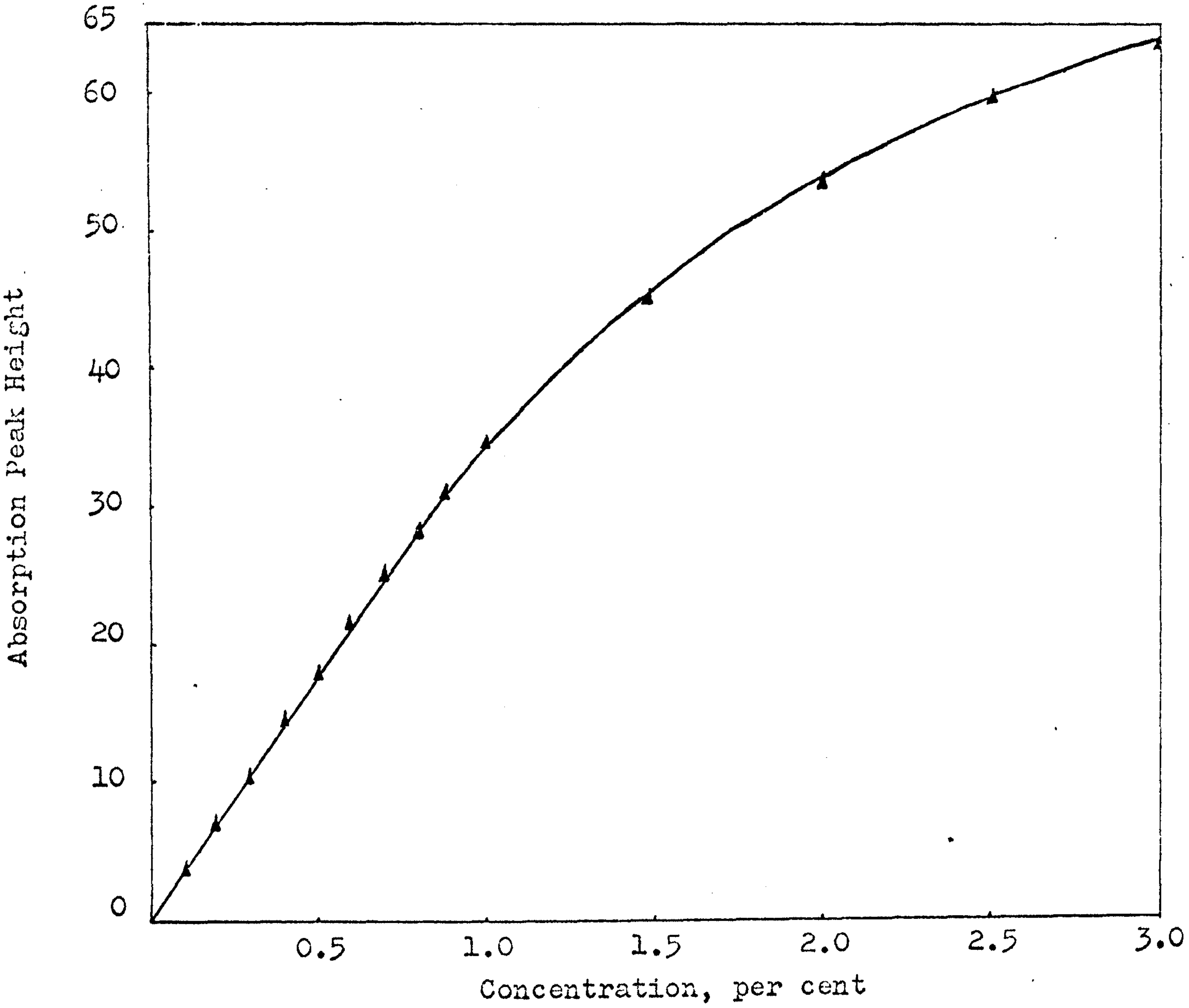


Figure 5 Absorbance versus per cent PAN in oil J

If bubbles were found, the procedure was repeated. Two pieces of plastic end sealings were then carefully squeezed into the ends of the cell. This ensured that the oil film remained in position without any further disturbance throughout the experiment. The unknown sample or the sample to be determined was charged to the sample cell in the same way as the pure solvent. Calibration curves, which were described in Section b, (1), were rerun each time a group of unknown samples were analyzed. Peak heights were then compared using the base line method (see below). A set of peak heights versus concentrations of additive data could be tabulated as Table II or Figure 4. From the calibration curve, a quantitative analysis of the unknown sample was obtained.

(3) Base Line Method

In the transmission curve of a sample of PAN in oil J, a base line AB (Figure 6) is drawn tangential to the transmission maxima on each side of the band. A perpendicular is then erected through the analytical wavelength until it intersects the base line. The absorbance is calculated using the lengths P_o and P as proportional to incident and transmitted light at that particular wavelength. According to Beer's law the concentration is proportional to the percentage of absorbance of the additive at the particular wavelength. It should be noted that the apparent amount of radiation absorbed is increased when the shoulders of the absorption band are raised (20). In order to take

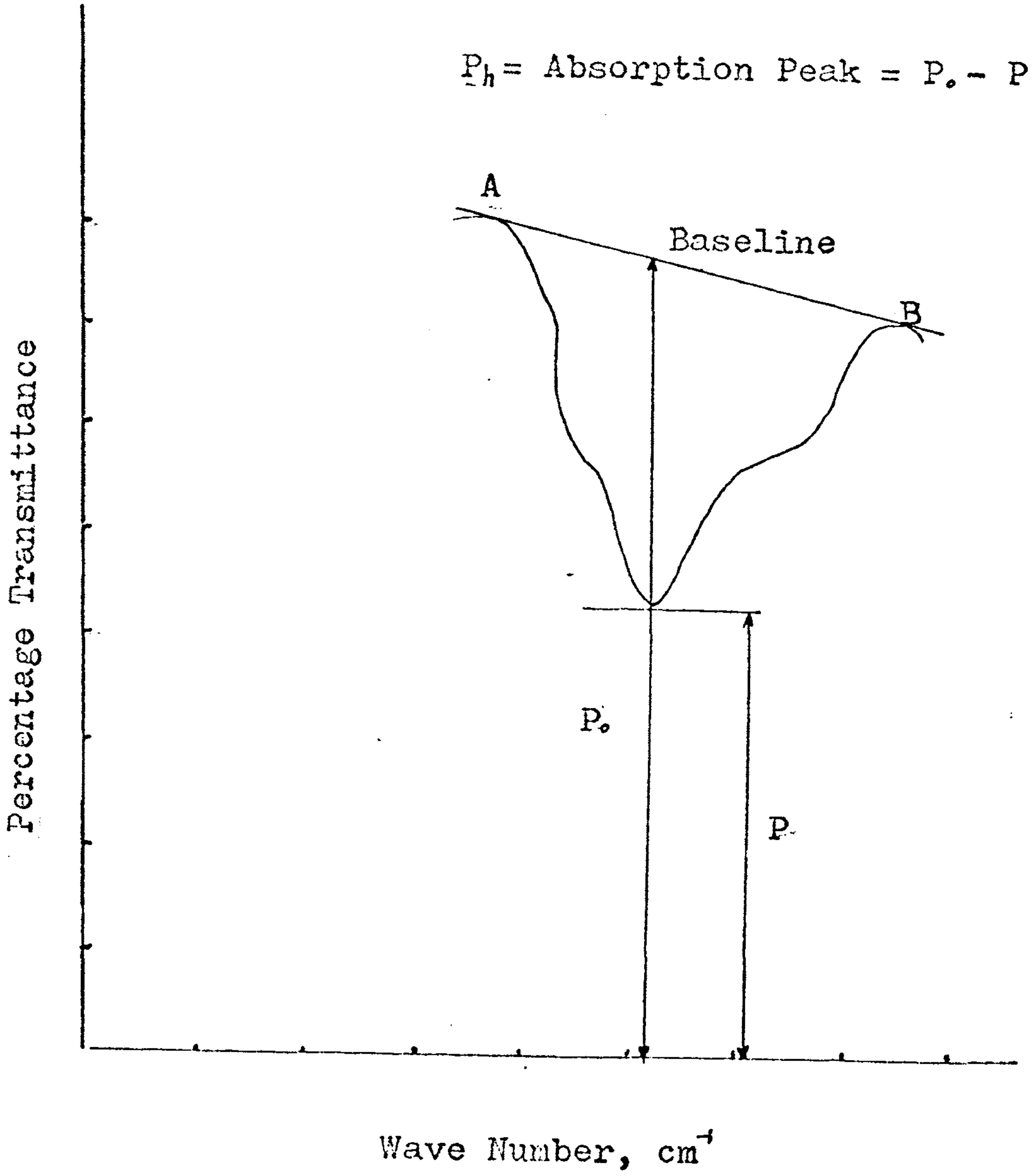


Figure 6 Technique of the Baseline Method

advantage of this, Robinson (21) suggested working at higher transmittances where the shoulders of the absorption band on each side of the analytical wavelength are near the 100 % transmission line.

IV. RESULTS AND DISCUSSION

A. Permeability Experiments on Grease Thickened with Silica Thickener and Aluminum Oxide

The results of the permeability measurements are listed in Table IX (Pages 69-77) and the calculated permeability coefficients are listed in Table V. Permeability coefficients varied from about 20.1 x 10^{-11} cm^2 to 168 x 10^{-11} cm^2. The average value of the standard deviation for these runs on each sample is 3.2 per cent compared with Lin's 2.8 per cent for Cab-O-Sil H-5 and M-5 greases.

Several trends are apparent in these results. First the level of the permeability coefficient is generally related to the worked penetration. Those greases with worked penetrations below about 300 had permeability coefficients of 20-35 x 10^{-11} cm^2. Those greases with worked penetrations in the range of 380-391 had permeability coefficients which ranged from 47-106. The two greases with worked penetrations of 408 and 409 had coefficients of 159 and 168 x 10^{-11} cm^2 respectively.

Also, within each series of thickeners (except for the uncompressed Aerosil), the permeability coefficient decreased with increase in surface area. Comparison of the QUSO F-22 results with Aerosil 2491 and Cab-O-Sil H-5 shows that differences in the level of permeability coefficient may be

TABLE VII

Summary of Permeability Results for Silica and Aluminum Oxide Greases at 77° F

Thickener	Slope $(\times 10^{-5})$	Permeability $(\times 10^{-11})$	Average $(\times 10^{-11})$
Aerosil Uncompressed	1.11	20.3	20.1
	1.13	20.6	
	1.06	19.4	
Aerosil MOX-170	2.50	47.0	46.8
	2.50	46.9	
	2.48	46.6	
Aerosil 2491	1.88	35.0	35.2
	2.03	37.7	
	1.78	33.0	
Aerosil 2491-380	1.77	31.7	32.6
	1.75	32.3	
	1.83	33.9	
Aluminum Oxide	8.06	174.	168.
	8.00	168.	
	7.70	161.	
Cab-O-Sil H-5(*)	-	21.2	20.6
		20.9	
		19.8	
Cab-O-Sil M-5(*)	-	24.1	22.9
		22.1	
		22.5	
Quso F-22	3.86	74.5	73.1
	3.78	71.8	
	3.80	73.1	
Quso G-32	5.28	105.	106.
	5.30	106.	
	5.35	106.	
Santocel Z	1.64	30.3	29.5
	1.56	28.6	
	1.61	29.7	
Santocel C	7.68	160.	159.
	7.63	160.	
	7.50	156.	

* Lin's Data (5)

obtained with silicas of roughly equal surface areas but prepared by different processes. The importance of the type of silica (pyrogel vs. hydrogel) on grease characteristics has been shown by Ewbank and his coworkers (18,22) in comparisons of the values of n, a measure of the concentration dependence of permeability.

The permeability coefficients observed with the aluminum oxide grease (168×10^{-11} cm^2) and the Santocel C grease (159×10^{-11} cm^2) are higher than any previously reported. These high coefficients suggest a loose holding of the mineral oil in a coarse gel structure which might be expected to permit excessive oil separation from the grease. After four months' storage, these two greases were the only ones which showed noticeable oil separation on their undisturbed surfaces (Table II).

B. Sorption Experiments on Greases Thickened with Silica and Aluminum Oxide

1. Sorption with Different PAN Concentrations in the Permeating Oil

The equilibrium results of the experiments in which permeating oil with varying concentrations of PAN was passed through a Cab-O-Sil H-5 thickened grease are shown in Table VI. and Figure 7. The equilibrium PAN concentrations in the grease exceeded those in the permeating oil by about 0.15 per cent at low PAN concentrations in the permeating oil and up to 0.59 per cent at 3.0 per cent PAN in the permeating oil based on PAN analysis of the exit oil. Thus, assuming uniform dispersion of additive in the oil phase at the same concentration as in the permeating oil, 0.03 gm to 0.13 gm of PAN must be associated with each gram of thickener, the amount increasing with the concentration of PAN in the oil. This additive must be held by surface forces on the thickener. Table VI also shows that direct infrared analyses of the greases for PAN gave good checks compared with the values estimated from mass balances obtained by analyses of the exit oil samples.*

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* These mass balances were corrected for PAN sorbed on the filter paper (see B 2).

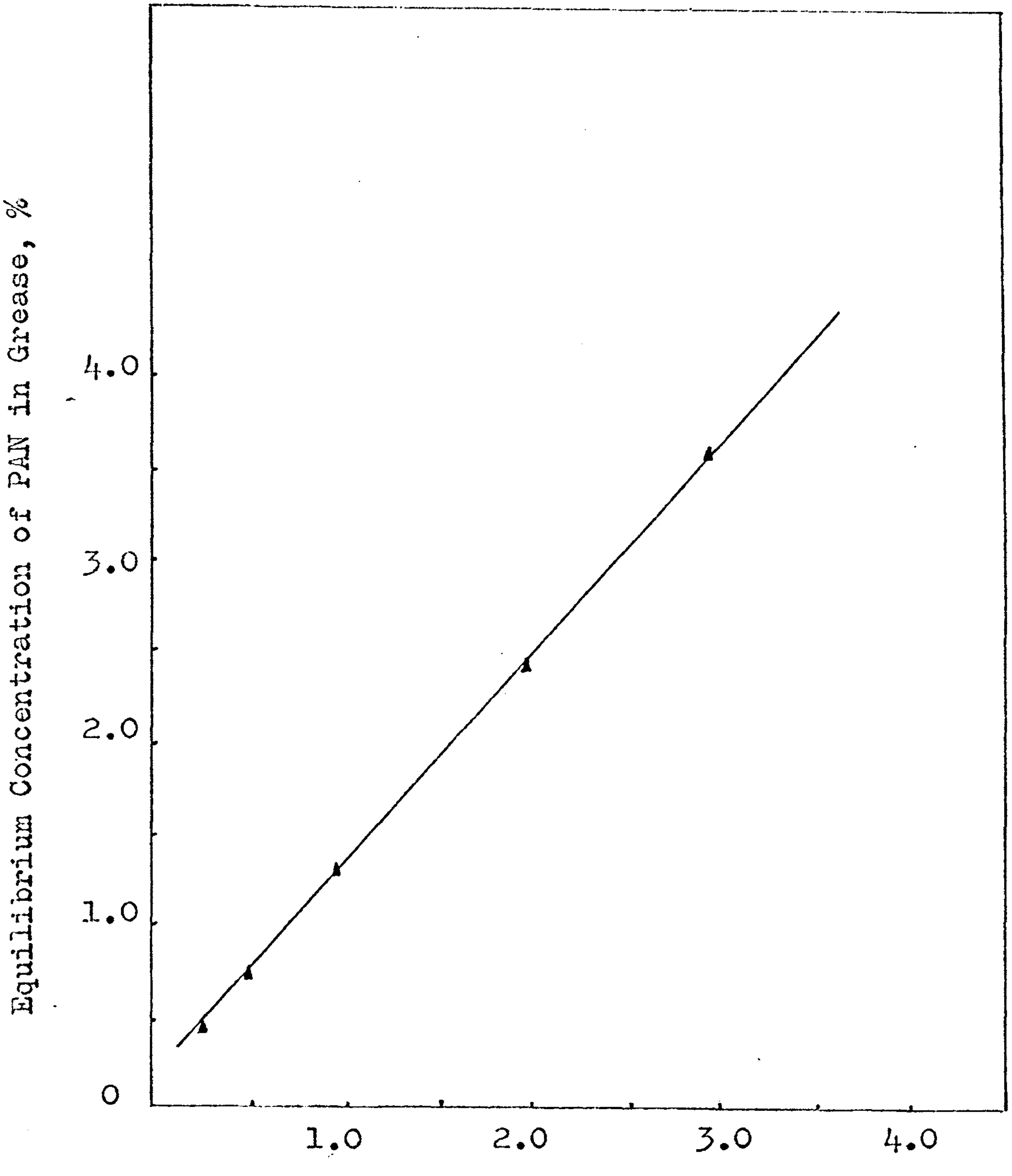


Figure 7 Equilibrium Concentration vs. Oil Concentration for Sorption Experiment

TABLE VI

Summary of Sorption and Extraction Results for Silica Grease (containing 6 % Cab-O-Sil H-5 Thickener)

% PAN in Permeating Oil			0.25	0.50	1.00	2.00	3.00
Sorption	% PAN in Grease at Equilibrium		0.40	0.75	1.30	2.47	3.59
		*	0.34	0.70	1.24	2.41	3.53
	Direct Analy. of Grease (% PAN)		0.36	0.71	1.26	2.43	3.55
	Vol. of Exit Oil at Equil. (cc)		24.9	23.4	22.5	17.2	16.8
	Ks		1.3	1.3	1.4	1.4	1.4
	Ks*		1.6	1.6	1.6	1.7	1.7
Extraction	% PAN in Grease at Equilibrium		-	0.13	0.15	0.07	0.13
	Direct Analy. of Grease (% PAN)		-	0.15	0.16	0.10	0.15
	Ke		-	1.3	1.4	1.4	1.4
	Ke*		-	1.6	1.6	1.7	1.7

* These mass balances were corrected for PAN sorbed on the filter paper.

2. Sorption of PAN Additive with Half, Normal and Double the Thickness of Silica Grease Cake

In order to check the possibility that the filter paper caused error in the calculated equilibrium concentration in the grease for the sorption experiment, half, normal and double thicknesses of Cab-O-Sil thickened grease cake were tested with oil containing one per cent of PAN. The results of the additive sorption experiments are shown in Table VII.

There was a difference in the final equilibrium concentration of PAN in these grease cakes calculated from the overall mass balances on PAN in the exit oil. It varied from 1.42 per cent in the half thickness to 1.30 per cent in the normal thickness and 1.26 per cent in the double thickness. The reason for these differences in the estimated values of the equilibrium concentration of PAN in the grease is apparently additive sorbed by the filter paper. Examination of the filter paper showed that it was slightly darker than the rest of the grease indicating a high PAN concentration. Grease sample scraped from the filter paper for all three cake thicknesses (estimate 1/25 of the normal grease cake thickness) contained 2.7 % PAN additive (approximately 0.0043 gm sorbed PAN associated with the filter paper). No significant difference in the amount of PAN on the filter papers was observed for the different grease sample thicknesses.

TABLE VII

Effect of Different Thickness of Grease Cake on Equilibrium Concentration in Grease for Sorption and Extraction Experiment

Grease Cake Thickness (cm) / Experiment		Half Thickness 0.238	Normal Thickness 0.476	Double Thickness 0.952
Sorption	Equilibrium Concentration (% PAN)	1.42	1.3	1.26
	Direct Grease Analysis (% PAN)	upper 1.30	1.28	1.26
		middle 1.29	1.27	1.25
		bottom 1.29	1.26	1.23
	Ks*	1.6	1.6	1.6
	Ks	1.4	1.4	1.4
Extraction	Equilibrium Concentration (% PAN)	0.13	0.15	0.18
	Direct Grease Analysis (% PAN)	upper 0.13	0.15	0.17
		middle 0.13	0.15	0.15
		bottom 0.13	0.15	0.15
	Ke	1.3	1.4	1.4
	Ke*	1.6	1.6	1.6

If the PAN associated with the filter paper is taken into account in the mass balances on the exit oil, the corrected average PAN concentration in the grease are 1.28 per cent, 1.24 per cent and 1.23 per cent for half, normal and double thicknesses of grease cake.

Direct infrared analysis of the grease sample from the half thickness sample cell gave 1.30 per cent PAN in the upper layer and 1.29 per cent in both the middle and the bottom layer. This shows that the PAN is uniformly distributed throughout the grease. For the normal thickness sample cell, the PAN concentration of the grease sample varied from 1.28 per cent in the upper layer to 1.27 per cent in the middle layer and 1.26 per cent in the bottom layer. For the double thickness sample cell, the PAN concentration varied from 1.26 per cent in the upper layer to 1.25 per cent in the middle and 1.23 per cent in the bottom layer. Thus, based on direct grease analysis, the equilibrium concentrations of the PAN varied only from an average of about 1.25 per cent to about 1.29 per cent as the cake thickness varied by a factor of 4. The results of the direct analyses of the greases are in good agreement with the values estimated from mass balances on PAN in the exit oil, after corrections were made for the PAN sorbed on the filter paper.

3. Sorption Experiments on Different Silica Greases and Aluminum Oxide Grease

The data for additive sorption in a number of greases with different silica thickeners and in an aluminum oxide thickener with one per cent PAN in the permeating oil are shown in Table X to Table XXXXI. The calculated results are shown in Table VIII.

The equilibrium concentration when oil containing one per cent of PAN was permeated through the grease increased from 1.07* per cent for Santocel C to 1.36 per cent of Santocel Z as the surface area increased from 130 m^2/gm to 280 m^2/gm. A similar but less pronounced trend with surface area was observed with the QUSO and the Cab-O-Sil greases. However, the effect of surface area on final PAN concentration was less significant in the Aerosil series. The PAN concentration in the aluminum oxide grease (0.96 per cent) indicates that there is little or no interaction between additive and this thickener.

* All equilibrium concentrations corrected for PAN associated with the filter paper.

TABLE VIII

Summary of Sorption and Extraction Results for Silica and Aluminum Oxide Grease

Thickener	Sorption			Extraction		
	Equil. Conc.# (% PAN)	Ks	Ks*	Final Equil. Conc. (% PAN)	Ke	Ke*
Santocel C	1.07	1.5	1.7	0.01	1.5	1.7
Santocel Z	1.36	1.3	1.6	0.13	1.3	1.6
Quso F-22	1.23	1.3	1.6	0.00	1.4	1.7
Quso G-32	1.20	1.4	1.7	0.10	1.4	1.7
Cab-O-Sil H-5	1.24	1.4	1.6	0.15	1.4	1.6
Cab-O-Sil M-5	1.13	1.4	1.7	0.13	1.4	1.7
Aerosil 2491	1.16	1.4	1.7	0.06	1.4	1.7
Aerosil 2491-380	1.15	1.4	1.6	0.04	1.4	1.6
Aerosil MOX-170	1.13	1.4	1.7	0.09	1.4	1.7
Aerosil Uncomp.	1.13	1.4	1.6	0.00	1.4	1.6
Aluminum Oxide	0.96	1.4	1.6	0.00	1.4	1.6

 # After correction for PAN associated with the filter paper.

C. Extraction of PAN Additive after Sorption Experiments

Extraction experiments using oil without additive were carried out on the Cab-O-Sil thickened grease samples which had reached equilibrium with the permeating oils containing 1.00 %, 2.00 % and 3.00 % PAN. The final equilibrium PAN concentrations are shown in Table VI. There was no significant difference among the final concentrations of additive in the greases. Infrared analyses for PAN in the greases again gave good checks against the PAN estimates based on the exit oil analyses.

Table VII shows the results of extraction experiments following the sorption of PAN additive with half, normal and double the thickness of Cab-O-Sil silica grease cake. There appears to be no significant difference among the final concentrations of the additive in the grease sample. Direct grease analyses again showed agreement with the PAN concentrations calculated from the mass balances. The grease sample scraped from the filter paper was analyzed and had the same concentration as other layers of the grease. This indicated that no appreciable amount of additive remained associated with the filter paper.

For the extraction after sorption experiments on different silica greases, only small amounts of PAN were retained in all the greases. (see Table X to Table XXXXI and Table VIII). The higher surface area Santocel Z thickener retained more PAN than the lower area Santocel C. For the Cab-O-Sils there is little difference and for the Aerosils and QUSO there is no apparent trend with surface area.

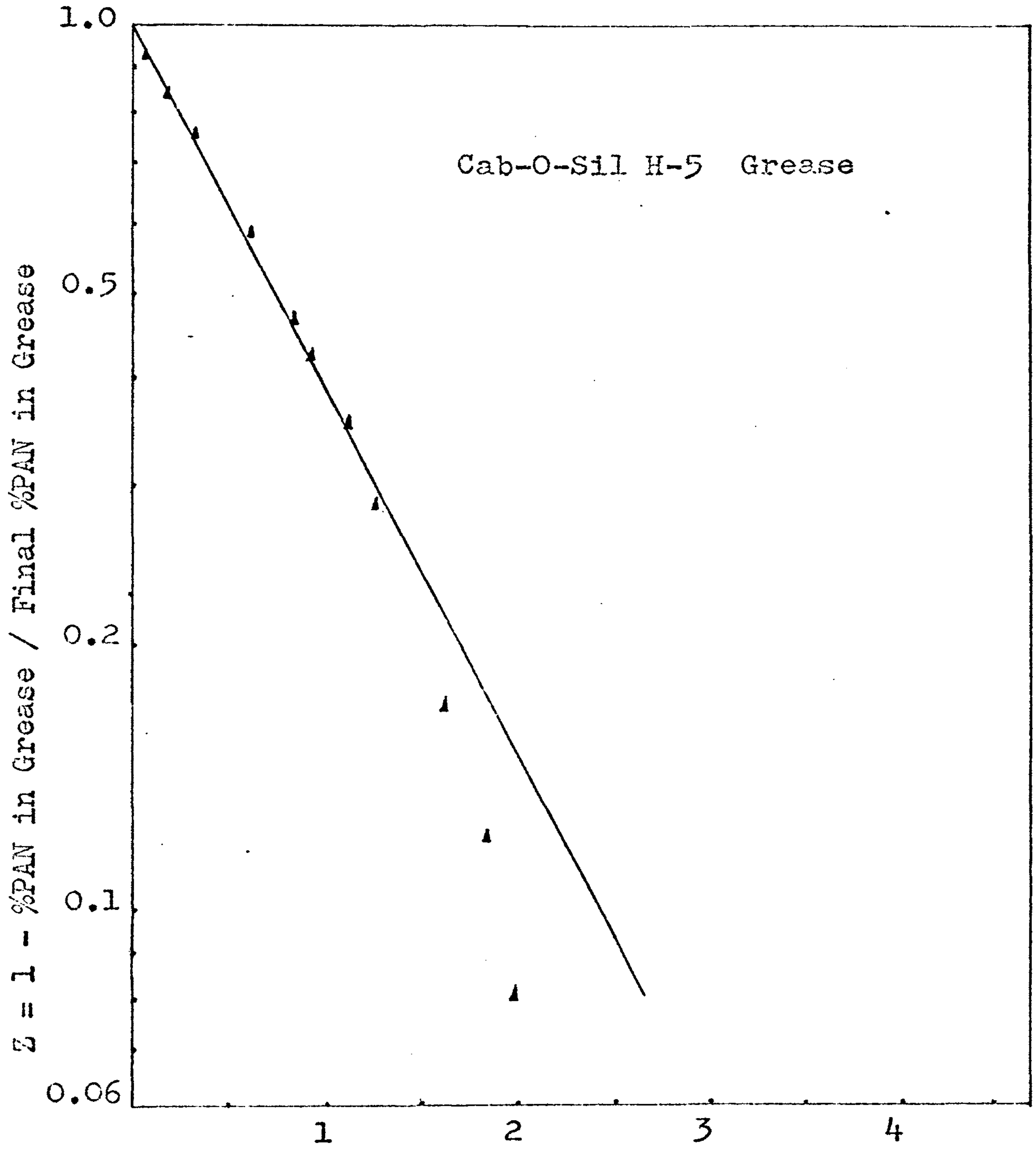
D. Rates of Sorption and Extraction of Additive

1. Sorption experiments

The sorption data were plotted as log[1 - (%PAN in grease / equilibrium % of PAN in grease)] vs. (volume of effluent oil / volume of grease sample) or log Z vs. X for the purpose of comparing the sorption rates. X is proportional to time as the flow rate for each grease was constant. Thus, the use of Vo/Vg permits comparison of equilibrium constants based on permeating oil volumes so that comparison between greases of different permeation rates can be made.

The semilogarithmic plots for all the greases studied were approximately linear with negative slopes at the start of the runs. A typical run is shown in Figure 8. The initial data appear to follow the first order rate equation $Z = e^{-KsX}$ where Ks is the absolute numerical value of the slope times 2.303. As Z becomes less than 0.1, any small error in either term leads to a large error in Z. The values of Ks determined from the initial slopes of the sorption data range from 1.3 to 1.5, independent of PAN concentration in the permeating oil, cake thickness or thickener type (Table VI, VII and VIII).

For lithium greases using several concentrations of PAN in the permeating oil, Zakin, Tu and Lin (6) reported values of Ks of 1.0 to 1.5 with the average 1.1. The values of Ks for similar experiments with their modified clay thickened greases were lower, ranging from 0.5 to 1.0 with an average



X = Volume of Effluent Oil/Volume of Grease

Figure 8 Reduced plot relating fraction of additive sorbed vs. volume of effluent oil with 1 % PAN (Slope of Ks) of 0.7 (6). Comparing the values of Ks for silica, lithium and Baragel greases, we find that the silica greases approach equilibrium more rapidly than the lithium and Baragel greases.

Although the initial Ks values were independent of PAN cpncentration in the oil, total volume of exit oil required for equilibrium concentrations of PAN in the silica greases decreased as the concentration of PAN in the permeating oil increased from about 25 cc at 0.25 per cent to about 17 cc at 3 per cent. This may be explained if we assume that the rate at which additive associates with the thickener is slow compared with additive exchange with the oil phase in the grease or with replacement of non-additive containing oil by additive containing oil. At higher PAN concentrations in the permeating oil, sorption on the thickener occurs more rapidly. If the surface sorption is the slower process and its contribution to the total PAN concentration in the grease is smaller than the oil phase contribution, the initial regions of plots of log (1 - Cgo/Cpo) vs. X (where Cgo is the PAN concentration in the oil phase of the grease and Cpo is the PAN concentration in the permeating oil) should give a rate constant descriptive of the fast process only.* Plots of this type gave rate constant, Ks*, values of about 1.6 and 1.7 for all runs (see Table VI, VII and VIII). A sample plot is shown in Figure 9. Linear regions generally extended to about the same X values but lower ordinate values than the plots from which Ks values were

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* Appendix B

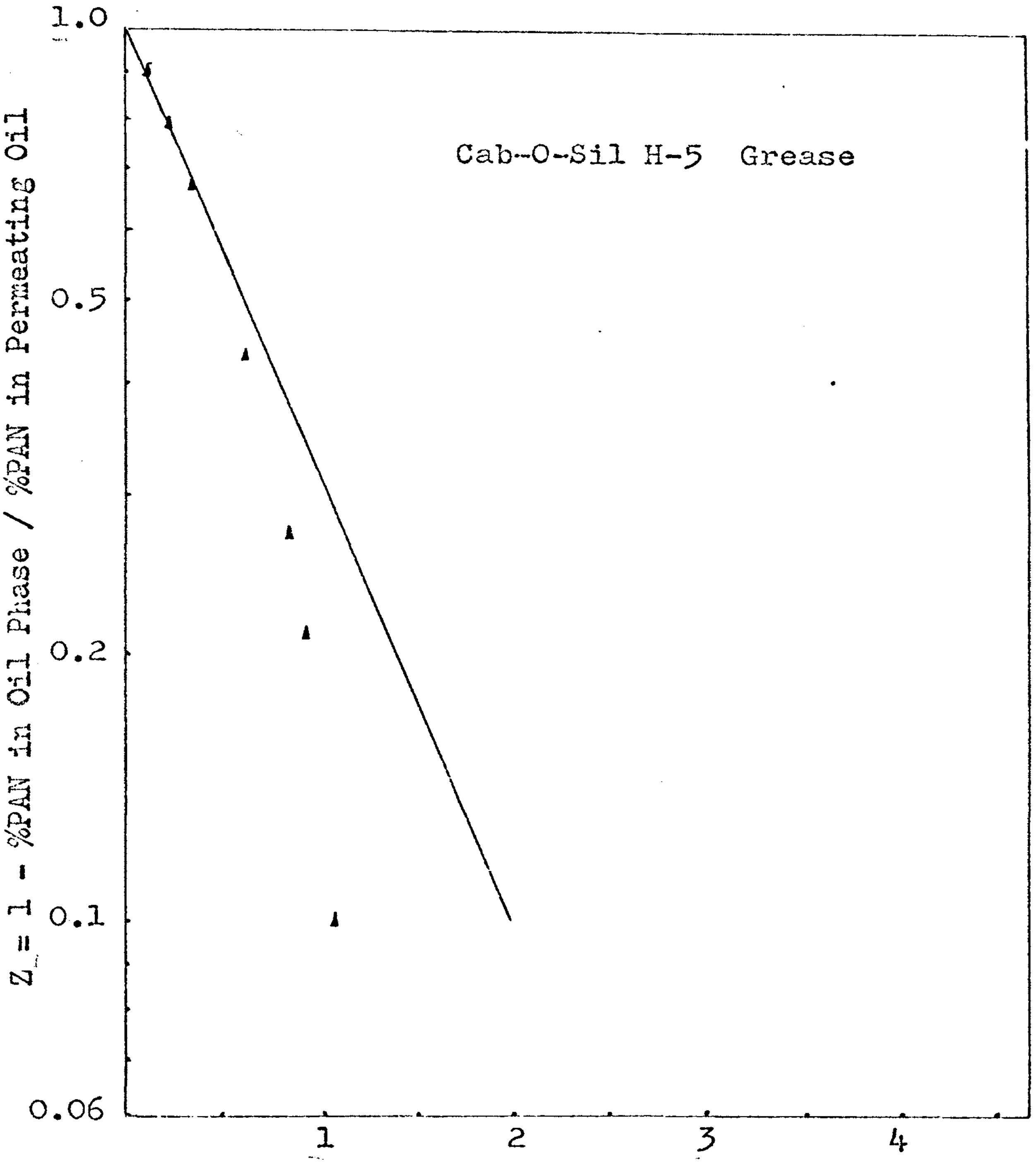

Figure 9 Reduced plot relating fraction of additive sorbed vs. volume of effluent oil with 1 % PAN (Slope of Ks*)

obtained. Recalculation of Lin's data gave average Ks* values of 1.4 for lithium greases and 0.9 for coated clay greases.

The data fall off faster than the initial rate line at high values of X. This may be a region where the rates of both processes are of the same magnitude. While it is true that the data in this region are subject to large errors because the small differences between two large concentrations appear in the ordinate, the deviations are consistently to the left of the extended initial rate line, suggesting that separate mechanisms of the type described above may be occuring.

Thus, Ks* values are only for the first effect described above, that is they measure the ability of permeating oil to replace the oil phase in the grease or to exchange additive with it. One could speculate that high Ks* values should be found in grease structures where the oil is held less "tightly" by the thickener and hence is more easily replaced or is at least more accèssible. In general these silica greases had lower thickener concentrations (and higher permeability coefficients) than the lithium and modified clay greases described above. The differences in the level of Ks* values could be due to differences in thickener characteristics and/or in thickener concentration. A study of Ks* values as a function of thickener concentration for a single thickener would be helpful in determining the importance of this variable.

2. Extraction experiments

The extraction data were plotted as log[(% PAN in grease - final % PAN) / (original % PAN in grease - final % PAN)] vs. (volume of effluent oil / volume of grease) or log Y vs. X. The semilogarithmic plots were also approximately linear with negative slopes at the start of the runs. A typical run is shown in Figure 10. The initial data appear to follow the first order rate equation $Y = e^{-KeX}$ where Ke is the absolute numerical value of the slope times 2.303. The values of Ke determined from the initial slopes of the extraction data range from 1.3 to 1.4. For lithium grease, the values of Ke varied from 1.0 to 1.1. For the modified clay base grease, the value of Ke varied from 0.8 to 1.0 (6).

The extraction data were also plotted as log (Cgo/Cgoi) vs. X where Cgo is the PAN concentration in oil phase of the grease at any time t and Cgoi is the original PAN concentration in oil phase of the grease.*

Plots of this type gave rate constant, Ke*, values of about 1.6 and 1.7 (see Table VI, VII and VIII). The average Ke and Ke* values for silica greases and the aluminum oxide grease are close to their average Ks and Ks* values. This same result was observed with the coated clay and lithium greases. Generally, this means that the rate limiting step at low X values is the same for sorption and extraction experiments.

* Appendix B

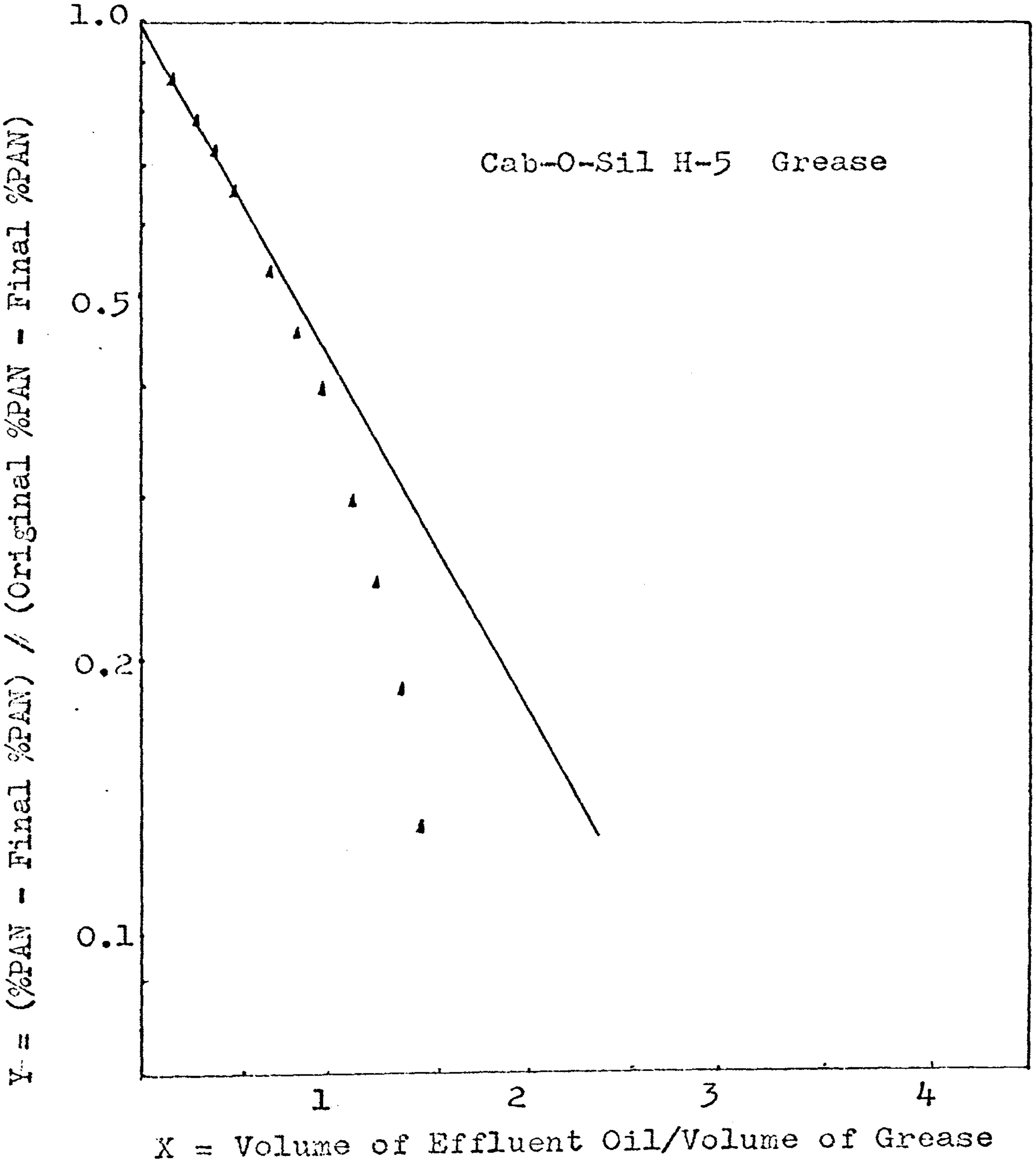

Figure 10 Reduced plot of fraction of additive removed vs. effluent oil volume

V. CONCLUSIONS

1. Permeability coefficients for greases thickened with 6 per cent of silica and aluminum oxide thickener varied from about 20.1 x 10^{-11} cm^2 to 168 x 10^{-11} cm^2 with the level of the permeability coefficient of a grease generally related to the level of the worked penetration.
2. In general for any thickener type the permeability coefficient decreased with increase in surface area of the thickener.
3. After sorption experiments with permeating oils containing 0.25 to 3.0 per cent of PAN through greases containing 6 per cent of Cab-O-Sil H-5 thickener, the amount of PAN associated with the thickener at equilibrium increased with the concentration of the additive in the permeating oil from 0.03 gm per gm to 0.13 gm per gm.
4. In sorption experiments with 1.0 per cent of PAN in the permeating oil passing through silica greases of 6 per cent thickener content, the equilibrium concentration generally increased with surface area for each silica thickener type. The effect was most noticeable for Santocel greases and least for Aerosil greases.

   There is little or no interaction between the PAN additive and aluminum oxide thickener.
5. Initial first order rate constants for additive concentration changes in the grease (Ks) and constants for concentration changes in the oil phase (Ks*) obtained from sorption data were independent of the type of silica

thickener. Initial constants for the extraction experiments (Ke and Ke*) were also independent of the type of silica thickener and were equal to the equivalent sorption rate constants.

The rate constants appear to be a function of thickener characteristics and/or thickener content and are independent of the thickness of the grease sample studied over a range of thickness of 4 : 1. The silica greases studied here approach equilibrium more rapidly than the lithium and coated clay greases of higher thickener content studied earlier.

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VII. APPENDIX

A. Sample Calculations

1. Permeability coefficient calculation

Permeability coefficient calculation of the sample grease is based on Darcy's law. A typical calculation with silica grease thickened with 6 % Aerosil 2491-380 thickener is shown below:

The equation used for this calculation is:

$$K = \frac{\nu L R_p^2/R_s^2}{g} \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

$$B = \frac{-K\, d(\ln h)}{dt} \;\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

where ν : kinematic viscosity of the oil = 219 CSTKS at 77° F.

Ap : area of pipette = 0.2623 cm^2

As : area of grease sample = 15.55 cm^2

R_p^2/R_s^2 : ratio of Ap/As = 0.01685

L : sample thickness = 0.476 cm

$$K = \frac{\nu L Ap/As}{g} = \frac{(219 \times 10^{-2})(0.476)(0.01685)}{980.66} = 1.79 \times 10^{-5}\, cm^2$$

From Equation (2) the plots of ln h vs. t should be linear. The slope of the line is:

$$\frac{d \ln h}{dt} = \frac{\ln 22.4 - \ln 10.3}{(12 - 0) \times 3600} = 1.77 \times 10^{-5}$$

The slope of the curve can best be calculated by a least squares analysis. A typical least squares program is shown in Section B.

$$B = (1.79 \times 10^{-5})(1.77 \times 10^{-5}) = 31.68 \times 10^{-11} \text{ cm}^2$$

This permeability coefficient includes the screens, filters and the grease sample. The permeability of the grease can be obtained by correction for the resistances of the screens and filters.

By running a blank experiment with the same screens and filters and with the oil J, but no grease sample, the permeability coefficient, B_o, of the screens and filters can be obtained.

$$B_o = 5.56 \times 10^{-5} \times \frac{\ln (29.1 / 10.2)}{(45 - 0) \times 60} = 9.5 \times 10^{-9} \text{ cm}^2$$

The total resistance is the sum of the individual resistances.

$$1/B = 1/B_o + 1/Bc$$

where B is the total permeability of the grease sample and Bc is the permeability of the grease itself.

$$Bc = \frac{B \times B_o}{B_o - B} = \frac{(31.68 \times 10^{-11})(9.5 \times 10^{-9})}{(9.5 \times 10^{-9}) - (31.68 \times 10^{-11})}$$

$$= 32.8 \times 10^{-11} \text{ cm}^2.$$

2. Sorption and extraction calculation

In the sorption and extraction experiments, the least squares method was used to smooth the PAN concentration vs. exit oil volume data and Simpson's rule was used to calculate the area under the curve. A computer program was written for the sorption experiments with 0.25, 0.5, 1.0, 2.0, 3.0 % PAN in the permeating oil and for the extraction calculations.

3. Sorption rate equation

Cgo = Conc. of PAN in oil phase of the grease.

Cpo = Conc. of PAN in the permeating oil.

Vo = Volume of exit oil.

Vg = Volume of grease.

For first order reaction

$$\frac{dCgo}{dt} = k\ (\ Cpo - Cgo\ )$$

$$\int \frac{dCgo}{Cpo - Cgo} = \int_0^t kdt$$

$$\ln\ (\ Cpo - Cgo\ ) = -kt + C$$

At t = 0. $\quad Cpo - Cgo = Cpo$

$$\therefore \ln \frac{Cpo - Cgo}{Cpo} = -kt = K\ (\frac{Vo}{Vg})$$

$$\therefore \ln(\ 1 - \frac{Cgo}{Cpo}) = K\ (\frac{Vo}{Vg})$$

4. Extraction Rate Equation.

Cgo = PAN Conc. in oil phase of the grease at time t.

Cgoi = Original PAN Conc. in oil phase of the grease.

Cpo = Conc. of PAN in the permeating oil.

$$\frac{dCgo}{dt} = k\ (\ Cgo - Cpo\ )$$

$$\int \frac{dCgo}{Cgo - Cpo} = \int_0^t kdt$$

$$\ln(Cgo - Cpo) = -kdt + C$$

At $t = 0.$

$$\ln(Cgoi) = C$$

$$\ln\left(\frac{Cgo - Cpo}{Cgoi}\right) = -kt = K \left(\frac{Vo}{Vg}\right)$$

$$Cpo \longrightarrow 0.$$

$$\ln\left(\frac{Cgo}{Cgoi}\right) = K \left(\frac{Vo}{Vg}\right)$$

B. Computer Program

```
 //OS  JOB CM120019,'FAN C S                 '  01/19/68 FORT 0002 0020 0000    19801
 **** JOB START.   DATE: 68.019, TIME OF DAY: 16:14:51
              C          SORPTION AND EXTRACTION CALCULATION
              C          USE LEAST SQUARES APPROXIMATING TECHNIQUE
              C          N= NUMBER OF DATAS
              C          M-1= DEGREE OF FUNCTION REQUIRE(FROM 2 TO 4 )
              C          WG= WEIGHT OF GREASE
              C          AE= % PAN IN PERMEATING OIL
              C          PAN = % PAN IN ORIGINAL GREASE
              C          X(I) = VOLUME OF EXIT OIL
              C          Y(I) = % PAN IN EXIT OIL
              C          BB(I) = TIME(HOURS)
                         DIMENSION X(50),Y(50),AP(50,50),AL(50),BA(50),B(50),A(50,50),S(50)
                         DIMENSION F(50),FS(50),FB(50),BF(50),BB(50),H(50),WW(50),VC(50)
                         DIMENSION FF(50),XS(50),ZZ(50),FM(50),T(50),NAME1(50),NAME2(50)
                         DO 99 KKK=1,50
                         READ(1,10) N,M
                         READ(1,11) WG,AE,PAN
                         READ(1,11) (X(I),Y(I),I=1,N)
                         READ(1,100) (BB(I),I=1,N)
                      71 WRITE(3,50) N,M,WG,AE,KKK,PAN
                      50 FORMAT('1',20X,I2,5X,I2,10X,2F8.4,10X,I3,10X,F5.3)
                      10 FORMAT(9X,I2,8X,I1)
                     100 FORMAT(5X,13F5.2)
                         W=1.0
                         SA1=0.0
                         SW1=0.0
                         DO 1 I=1,N
                         XS(I)=X(I)/WG
                         SA1=SA1+W*X(I)
                         SW1=SW1+W
                       1 AP(1,I)=1.0
                         AL(1)=SA1/SW1
                         SA2=0.0
                         SW2=0.0
                         SB1=0.0
                         DO 20 I=1,N
                         AP(2,I)=X(I)-AL(1)
                         SA2=SA2+W*X(I)*(AP(2,I)**2)
                         SW2=SW2+W*(AP(2,I)**2)
                      20 SB1=SB1+W*(AP(1,I)**2)
                         AL(2)=SA2/SW2
                         BA(1)=SW2/SB1
                         IF(M-3)23,24,24
                      24 DO 2 J=3,M
                         SA=0.0
                         SB=0.0
                         SW=0.0
```

```
      DO 3 I=1,N
      AP(J,I)=(X(I)-AL(J-1))*AP(J-1,I)-BA(J-2)*AP(J-2,I)
      SA=SA+W*X(I)*(AP(J,I)**2)
      SW=SW+W*(AP(J,I)**2)
    3 SB=SB+W*(AP(J-1,I)**2)
      AL(J)=SA/SW
    2 BA(J-1)=SW/SB
   23 DO 4 J=1,M
      SC=0.0
      SD=0.0
      DO 5 I=1,N
      SC=SC+W*Y(I)*AP(J,I)
    5 SD=SD+W*(AP(J,I)**2)
    4 B(J)=SC/SD
      WRITE(3,12)
      DO 7 I=1,M
    7 A(I,I)=1.0
      A(2,1)=-AL(1)
      IF(M-3)25,26,26
   26 DO 6 I=3,M
      A(I,1)=-AL(I-1)*A(I-1,1)-BA(I-2)*A(I-2,1)
    6 A(I,I-1)=-AL(I-1)*A(I-1,I-1)+A(I-1,I-2)
      IF(M-4)30,31,31
   30 GO TO 28
   31 DO 9 I=4,M
    9 A(I,2)=-AL(I-1)*A(I-1,2)+A(I-1,1)-BA(I-2)*A(I-2,2)
      DO 18 I=5,M
   18 A(I,3)=-AL(I-1)*A(I-1,3)+A(I-1,2)-BA(I-2)*A(I-2,3)
   25 IF(M-2)27,28,28
   28 DO 22 I=2,M
      A(1,I)=0.
      A(2,I+1)=0.
      A(3,I+2)=0.
   22 A(4,I+3)=0.
   27 DO 19 J=1,M
   19 WRITE(3,13) (A(J,II),II=1,J)
      DO 8 IK=1,M
      C=0.0
      DO 8 IJ=1,M
      C=C+B(IJ)*A(IJ,IK)
    8 S(IK)=C
      WRITE(3,21)
      WRITE(3,14) (S(KK),KK=1,M)
   12 FORMAT(///20X,'X0',16X,'X1',16X,'X2',16X,'X3',16X,'X4')
   13 FORMAT(8X,5F18.6)
   21 FORMAT(///19X,'C1',16X,'C2',16X,'C3',16X,'C4',16X,'C5')
   14 FORMAT(8X,5F18.6)
   11 FORMAT(4E18.8)
```

```
      WRITE(3,101)
  101 FORMAT('1'///46X,'TABLE'///////6X89(1H*))
      WRITE(3,104)
  104 FORMAT(6X1H*,'SAMPLE ',1H*,'  TIME ',1H*,' TOTAL VOL ',1H*,' % ADD
     1ITIVE',1H*,'% ADDITIVE ',1H*,'V.EXIT.OIL ',1H*,'       #    ',1H*,'
     2    #     ',1H*)
      WRITE(3,105)
  105 FORMAT(6X1H*,'  NO   ',1H*,7X1H*,' EXIT  OIL ',1H*,'        IN    ',1
     1H*,'    IN    #',1H*,'----------#',1H*,'      F     ',1H*,'       Y
     1    ',1H*)
      WRITE(3,106)
  106 FORMAT(6X1H*,7X1H*,' (HOUR)',1H*,'    (C C)    ',1H*,'  EXIT OIL ',1
     1H*,'  GREASE   ',1H*,'VOL.GREASE ',1H*,11X1H*,11X1H*)
      WRITE(3,107)
  107 FORMAT(6X,89(1H*))
C     APPLIED SIMPSION'S RULE
      DO 70 I=1,N
      H(I)=(X(I)-0.)/20.
      XX=0.
      NN=21
      DO 114 J=1,21
      IF(M-5)41,40,40
   41 S(5)=0.
      IF(M-4)43,40,40
   43 S(4)=0.
      IF(M-3)45,40,40
   45 S(3)=0.
   40 F(J)=S(1)+S(2)*XX+S(3)*XX**2+S(4)*XX**3+S(5)*XX**4
  114 XX=XX+H(I)
      WW(I)=0.
      NM=19
      DO 115 J=1,NM,2
  115 WW(I)=WW(I)+F(J)+4.*F(J+1)+F(J+2)
   70 FS(I)=WW(I)*H(I)/3.
      IF(AF-4.)66,68,68
   66 IF(AF-1.)60,61,62
   60 DO 74 I=1,N
   74 FB(I)=X(I)*0.5-FS(I)
      GO TO 73
   61 DO 75 I=1,N
   75 FB(I)=X(I)-FS(I)
      GO TO 73
   62 IF(AF-2.)63,63,64
   63 DO 76 I=1,N
   76 FB(I)=X(I)*2.-FS(I)
      GO TO 73
   64 IF(AF-3.)65,65,68
   65 DO 77 I=1,N
```

```
   77 FB(I)=Y(I)*3.-FS(I)
   73 DO 78 I=1,N
      BF(I)=FB(I)*0.9/WG
      J=I-1
      IF(I-2)78,80,80
   80 IF(BF(I)-BF(J))81,78,78
   81 BF(I)=BF(J)
   78 CONTINUE
      DO 117 I=1,N
      FM(I)=S(1)+S(2)*X(I)+S(3)*X(I)**2+S(4)*X(I)**3+S(5)*X(I)**4
      FF(I)=BF(I)/BF(N)
  117 ZZ(I)=1.-FF(I)
      GO TO 69
   68 Y(I)=PAN
      DO 116 I=1,N
      FM(I)=S(1)+S(2)*X(I)+S(3)*X(I)**2+S(4)*X(I)**3+S(5)*X(I)**4
      BF(I)=PAN-FS(I)*0.9/WG
      J=I-1
      IF(I-2)116,82,82
   82 IF(BF(I)-BF(J))116,83,83
   83 BF(I)=BF(J)
  116 CONTINUE
      DO 118 I=1,N
      FF(I)=BF(I)/PAN
  118 ZZ(I)=(BF(I)-BF(N))/(Y(I)-BF(N))
   69 DO 109 I=1,N
  109 WRITE(3,102) I,BB(I),X(I),Y(I),BF(I),XS(I),FF(I),ZZ(I)
  102 FORMAT(6X1H*,2(7X1H*),6(11X1H*),/6X1H*,2X,I2,3X1H*,F6.2,1X1H*,6(F8
     1.2,3X1H*))
      WRITE(3,103)
  103 FORMAT(6X,89(1H*)//28X,'F=%PAN IN GREASE / ORIGINAL % PAN IN GREAS
     1E',/28X,'Y=(%PAN - FINAL %PAN)/(ORIGINAL %PAN - FINAL %PAN)')
      M=M+1
      IF(M-5)72,72,99
   72 GO TO 71
   99 CONTINUE
      STOP
      END
```

C. Tables of Data

TABLE IX A.

DATA FOR PERMEABILITY TESTS ON SILICA GREASE
(6 % SANTOCEL SILICA Z THICKENER)

TIME (hrs)	RUN 1	RUN 2 HEIGHT (cm)	RUN 3
0	18.20	22.50	25.00
0.5	17.70	22.00	24.30
1	17.10	21.40	23.60
1.5	16.70	20.70	22.80
2	16.10	20.10	22.30
2.5	15.70	19.60	21.80
3	15.20	19.00	21.00
4	14.30	18.00	19.80
5	13.50	17.00	18.70
6	12.80	16.00	17.60
7	12.00	15.10	16.70
8	11.30	14.30	15.70
9	10.70	13.50	14.80
10	10.10	12.80	14.00

TABLE IX B.

DATA FOR PERMEABILITY TESTS ON SILICA GREASE
(6 % SANTOCEL SILICA C THICKENER)

TIME (hrs)	RUN 1	RUN 2 HEIGHT (cm)	RUN 3
0	22.40	26.50	28.10
1	18.50	20.00	21.80
2	14.00	15.20	16.70
3	10.60	11.50	12.70
4	8.10	8.80	9.80
5	6.20	6.70	7.40
6	4.70	5.10	5.60
7	3.60	3.80	4.30
8	2.70	2.90	3.30
9	2.00	2.20	2.50
10	1.55	1.70	1.90

TABLE IX C.

DATA FOR PERMEABILITY TESTS ON SILICA GREASE
(6 % QUSO SILICA F-22 THICKENER)

TIME (hrs)	RUN 1	RUN 2 HEIGHT (cm)	RUN 3
0	22.50	28.50	26.80
0.5	20.90	26.70	24.80
1	19.500	24.80	23.20
1.5	18.50	23.50	21.60
2	17.10	21.90	20.10
2.5	15.70	20.50	18.80
3	14.80	19.20	17.70
4	13.00	16.70	15.60
5	11.10	14.60	13.50
6	9.70	12.60	11.80
7	8.50	11.00	10.30
8	7.40	9.50	8.90
9	6.40	8.35	7.80
10	5.60	7.30	6.80

TABLE IX D.

DATA FOR PERMEABILITY TESTS ON SILICA GREASE (6 % QUSO SILICA PG-32 THICKENER)

TIME (hrs)	RUN 1	RUN 2 HEIGHT (cm)	RUN 3
0	24.80	23.60	21.90
0.5	22.60	20.00	21.40
1	20.70	19.50	18.20
1.5	18.70	17.70	16.50
2	17.10	16.20	14.90
2.5	15.40	14.70	13.60
3	14.00	13.30	12.40
3.5	12.80	12.10	11.30
4	11.70	10.90	10.20
4.5	10.60	9.30	10.00
5	9.60	9.10	8.40
5.5	8.70	7.70	8.20
6	8.00	7.50	7.00
7	6.60	6.20	5.70
8	5.40	5.10	4.70
9	4.50	4.20	3.90
10	3.70	3.50	3.20

TABLE IX E.

DATA FOR PERMEABILITY TESTS ON SILICA GREASE
(6 % AEROSIL UNCOMPRESSED THICKENER)

TIME (hrs)	RUN 1	RUN 2 HEIGHT (cm)	RUN 3
0.	19.30	26.90	24.80
1	18.40	25.81	23.70
2	17.75	25.00	22.70
2.5	17.40	24.34	22.31
3	17.18	24.02	21.82
4	16.49	22.70	20.80
5	15.90	21.90	20.02
6	15.31	21.03	19.30
7	14.60	20.11	19.02
8	14.11	19.40	17.80
9	13.52	18.60	17.11
10	13.01	17.90	16.99

TABLE IX F.

Data for Permeability Tests on Silica Grease
(6 % Aerosil 2491-380 Thickener)

Time (hrs)	Run 1	Run 2	Run 3
		Height (cm)	
0	22.4	21.2	25.2
1	21.5	19.9	23.6
2	20.0	18.7	22.1
3	18.6	17.5	20.7
4	17.6	16.5	19.3
5	16.7	15.4	18.1
6	16.0	14.7	16.9
7	14.6	13.6	15.8
8	13.6	12.7	14.8
9	12.8	12.0	13.8
10	11.9	11.3	13.0

TABLE IX G.

Data for Permeability Tests on Silica Grease
(6 % Aerosil 2491 Thickener)

Time (hrs)	Run 1	Run 2 Height (cm)	Run 3
0	21.4	23.9	22.8
1	20.1	22.2	21.3
2	18.6	20.7	20.0
3	17.6	19.5	18.5
4	16.5	18.1	17.3
5	15.4	16.8	16.2
6	14.3	15.7	15.1
7	13.5	14.7	14.2
8	12.6	13.8	13.8
9	11.7	12.3	12.8
10	10.8	11.5	12.0

TABLE IX H.

Data for Permeability Tests on Silica Grease
(6 % Aerosil MOX-170 Thickener)

Time (hrs)	Run 1	Run 2 Height (cm)	Run 3
0	21.6	22.2	23.2
1	19.7	20.1	21.4
2	17.9	18.6	19.8
3	16.5	16.7	17.8
4	15.1	15.4	16.3
5	13.8	14.1	14.9
6	12.5	12.8	13.5
7	11.6	11.7	12.4
8	10.4	10.7	11.4
9	9.7	9.9	10.8
10	8.8	9.1	9.5

TABLE IX I.

Data for Permeability Tests on Aluminum Grease (6 % Aluminum Oxide Thickener)

Time (hrs)	Run 1	Run 2 Height (cm)	Run 3
0	26.30	23.30	24.80
1	20.20	17.70	18.70
2	15.50	13.50	14.20
3	11.20	10.00	10.70
4	8.25	7.55	8.10
5	6.25	5.70	6.10
6	4.65	4.35	4.65
7	3.67	3.30	3.50
8	2.60	2.45	2.60
9	2.00	1.80	2.00
10	1.50	1.40	1.50

TABLE X

SORPTION BY SILICA GREASE

(6 % SANTOCEL C THICKENER--1 % PAN IN PERMEATING OIL)

SAMPLE NO	TIME (HOUR)	TOTAL VOL EXIT OIL (C C)	% ADDITIVE IN EXIT OIL	% ADDITIVE IN GREASE	#V. EXIT. OIL / VOL. GREASE#	# F	# Z
1	2.25	1.60	0.0	0.23	0.21	0.20	0.80
2	4.00	2.90	0.01	0.38	0.37	0.34	0.66
3	6.00	4.00	0.05	0.52	0.53	0.46	0.54
4	14.80	7.70	0.13	0.85	1.03	0.75	0.25
5	19.55	9.50	0.43	0.96	1.27	0.85	0.15
6	22.30	10.90	0.74	1.03	1.45	0.91	0.09
7	25.00	12.30	0.91	1.08	1.64	0.95	0.05
8	27.50	13.80	0.98	1.12	1.84	0.99	0.01
9	29.20	15.00	0.99	1.13	2.00	1.00	0.0
10	38.70	18.60	1.00	1.13	2.49	1.00	0.0

F = %PAN IN GREASE / FINAL %PAN IN GREASE

Z = 1-(%PAN IN GREASE / FINAL %PAN IN GREASE)

: CALCULATED FROM SMOOTHED OIL CONCENTRACTION VS OIL VOLUME DATA

TABLE XI

EXTRACTION AFTER SORPTION

(6 % SANTOCEL C THICKENER--1.13 % PAN IN GREASE)

SAMPLE NO	TIME (HOUR)	TOTAL VOL EXIT OIL (C C)	% ADDITIVE IN EXIT OIL	% ADDITIVE IN GREASE	V.EXIT.OIL / VOL.GREASE	F	Y
1	0.0	0.0	1.13	1.13	0.0	1.00	1.00
2	3.00	1.25	1.00	0.98	0.16	0.87	0.87
3	5.80	2.95	0.93	0.79	0.38	0.70	0.70
4	8.80	5.15	0.88	0.57	0.66	0.51	0.50
5	13.50	7.50	0.81	0.37	0.96	0.33	0.32
6	17.80	9.45	0.65	0.24	1.21	0.21	0.20
7	20.60	10.60	0.40	0.17	1.36	0.15	0.15
8	23.50	11.90	0.13	0.11	1.53	0.10	0.09
9	26.80	14.30	0.06	0.04	1.83	0.03	0.02
10	30.80	16.90	0.01	0.01	2.17	0.01	0.0
11	32.40	18.00	0.0	0.01	2.31	0.01	0.0

F = %PAN IN GREASE / ORIGINAL %PAN IN GREASE
Y = (%PAN - FINAL %PAN) / (ORIGINAL %PAN - FINAL %PAN)

TABLE XII

SORPTION BY SILICA GREASE

(6 % SANTOCEL Z THICKENER--1 % PAN IN PERMEATING OIL)

SAMPLE NO	TIME (HOUR)	TOTAL VOL EXIT OIL (C C)	% ADDITIVE IN EXIT OIL	% ADDITIVE IN GREASE	V. EXIT. OIL / VOL. GREASE	F	Z
1	0.0	0.0	0.0	0.0	0.0	0.0	1.00
2	6.00	1.50	0.0	0.20	0.21	0.14	0.86
3	13.50	3.70	0.0	0.48	0.52	0.34	0.66
4	18.20	5.20	0.03	0.65	0.73	0.46	0.54
5	23.10	6.60	0.12	0.80	0.92	0.56	0.44
6	25.50	7.20	0.16	0.85	1.00	0.60	0.40
7	29.00	8.10	0.24	0.94	1.13	0.66	0.34
8	33.20	9.20	0.32	1.03	1.28	0.72	0.28
9	36.00	10.10	0.40	1.10	1.41	0.77	0.23
10	40.10	11.10	0.52	1.17	1.55	0.82	0.18
11	44.30	12.50	0.68	1.25	1.74	0.88	0.12
12	49.20	13.90	0.76	1.32	1.94	0.93	0.07
13	54.50	15.40	0.86	1.38	2.15	0.97	0.03
14	58.00	16.50	0.90	1.41	2.30	0.99	0.01
15	62.10	17.60	0.95	1.42	2.45	1.00	0.00
16	64.40	18.20	0.97	1.42	2.54	1.00	0.0
17	67.50	19.30	0.99	1.42	2.69	1.00	0.0
18	69.50	20.00	1.00	1.42	2.79	1.00	0.0

F = %PAN IN GREASE / FINAL %PAN IN GREASE
Z = 1 - (%PAN IN GREASE / FINAL %PAN IN GREASE)

TABLE XIII

EXTRACTION AFTER SORPTION
(6 % SANTOCEL Z THICKENER--1.42 % PAN IN GREASE)

SAMPLE NO	TIME (HOUR)	TOTAL VOL EXIT OIL (C C)	% ADDITIVE IN EXIT OIL	% ADDITIVE IN GREASE	V.EXIT.OIL / VOL.GREASE	F	Y
1	0.0	0.0	1.42	1.42	0.0	1.00	1.00
2	4.10	1.50	0.96	1.23	0.21	0.87	0.85
3	7.10	2.60	0.92	1.10	0.36	0.78	0.75
4	12.00	4.20	0.86	0.93	0.59	0.65	0.62
5	22.50	7.45	0.72	0.62	1.04	0.44	0.38
6	28.40	8.65	0.61	0.53	1.21	0.37	0.31
7	32.30	9.85	0.55	0.44	1.37	0.31	0.25
8	36.40	11.35	0.42	0.35	1.58	0.25	0.17
9	47.10	12.95	0.31	0.27	1.81	0.19	0.11
10	55.40	15.95	0.15	0.16	2.22	0.11	0.03
11	60.05	18.45	0.05	0.13	2.57	0.09	0.00
12	71.05	19.95	0.0	0.12	2.78	0.09	0.0

F = %PAN IN GREASE / ORIGINAL %PAN IN GREASE
Y = (%PAN - FINAL %PAN) / (ORIGINAL %PAN - FINAL %PAN)

TABLE XIV

SORPTION BY SILICA GREASE

(6 % QUSO SILICA G-32 THICKENER--1 % PAN IN PERMEATING OIL)

SAMPLE NO	TIME (HOUR)	TOTAL VOL EXIT OIL (C C)	% ADDITIVE IN EXIT OIL	% ADDITIVE IN GREASE	V. EXIT OIL / VOL. GREASE	F	Y
1	2.30	1.90	0.0	0.28	0.26	0.23	0.77
2	5.30	3.80	0.02	0.53	0.52	0.43	0.57
3	7.90	5.55	0.07	0.72	0.76	0.58	0.42
4	9.50	6.80	0.14	0.84	0.93	0.68	0.32
5	18.90	10.90	0.62	1.12	1.49	0.90	0.10
6	23.15	12.50	0.86	1.18	1.71	0.95	0.05
7	25.65	13.80	0.93	1.22	1.89	0.98	0.02
8	29.50	15.60	0.98	1.24	2.14	1.00	0.0
9	31.80	17.80	1.00	1.24	2.44	1.00	0.0

F = %PAN IN GREASE / FINAL %PAN IN GREASE

Z = 1 - (%PAN IN GREASE / FINAL %PAN IN GREASE)

TABLE XV

EXTRACTION AFTER SORPTION

(6 % QUSO SILICA G-32 THICKENER--1.26 % PAN IN GREASE)

SAMPLE NO	TIME (HOUR)	TOTAL VOL EXIT OIL (C.C)	% ADDITIVE IN EXIT OIL	% ADDITIVE IN GREASE	V.EXIT.OIL / VOL.GREASE	F	Y
1	0.0	0.0	1.26	1.26	0.0	1.00	1.00
2	4.00	2.35	1.00	0.95	0.34	0.76	0.74
3	7.50	4.80	0.83	0.69	0.69	0.55	0.51
4	11.30	7.60	0.60	0.45	1.09	0.35	0.30
5	13.30	8.90	0.46	0.36	1.28	0.28	0.22
6	23.30	12.90	0.22	0.17	1.84	0.13	0.06
7	28.10	14.70	0.05	0.12	2.11	0.10	0.02
8	32.10	16.90	0.01	0.10	2.42	0.08	0.0
9	34.10	18.00	0.0	0.10	2.58	0.08	0.0

F = %PAN IN GREASE / ORIGINAL %PAN IN GREASE
Y = (%PAN - FINAL %PAN) / (ORIGINAL %PAN - FINAL %PAN)

TABLE XVI

SORPTION BY SILICA GREASE

(6 % QUSO SILICA F-22 THICKENER--1 % PAN IN PERMEATING OIL)

SAMPLE NO	TIME (HOUR)	TOTAL VOL EXIT OIL (C C)	% ADDITIVE IN EXIT OIL	% ADDITIVE IN GREASE	V.EXIT.OIL / VOL.GREASE	F	Z
1	0.0	0.0	0.0	0.0	0.0	0.0	1.00
2	6.50	1.50	0.0	0.20	0.20	0.15	0.85
3	10.40	2.40	0.0	0.31	0.33	0.24	0.76
4	15.00	3.40	0.01	0.42	0.46	0.33	0.67
5	22.10	5.00	0.12	0.59	0.68	0.45	0.55
6	29.20	6.60	0.26	0.74	0.90	0.57	0.43
7	34.40	8.00	0.36	0.85	1.09	0.66	0.34
8	40.50	9.20	0.44	0.94	1.25	0.73	0.27
9	47.30	10.80	0.52	1.04	1.47	0.80	0.20
10	54.40	12.40	0.64	1.12	1.69	0.87	0.13
11	61.30	14.00	0.77	1.19	1.91	0.92	0.08
12	69.50	15.50	0.84	1.24	2.11	0.96	0.04
13	77.40	17.20	0.93	1.27	2.34	0.98	0.02
14	91.00	20.40	0.99	1.29	2.78	1.00	0.0
15	93.30	21.00	1.00	1.29	2.86	1.00	0.0

F = %PAN IN GREASE / FINAL %PAN IN GREASE
Z = 1 - (%PAN IN GREASE / FINAL %PAN IN GREASE)

TABLE XVII

EXTRACTION AFTER SORPTION

(6 % QUSO SILICA F-22 THICKENER--1.29 % PAN IN GREASE)

SAMPLE NO	TIME (HOUR)	TOTAL VOL EXIT OIL (C.C)	% ADDITIVE IN EXIT OIL	% ADDITIVE IN GREASE	V. EXIT OIL / VOL. GREASE	F	Y
1	0.0	0.0	1.00	1.29	0.0	1.00	1.00
2	4.00	1.50	0.97	1.10	0.21	0.85	0.85
3	7.00	2.50	0.93	0.99	0.34	0.77	0.77
4	12.00	4.10	0.85	0.82	0.56	0.64	0.64
5	23.00	7.50	0.74	0.48	1.03	0.37	0.37
6	28.50	8.50	0.65	0.40	1.16	0.31	0.31
7	32.50	9.90	0.50	0.30	1.36	0.23	0.23
8	37.00	11.50	0.40	0.21	1.58	0.16	0.16
9	47.00	13.00	0.30	0.14	1.78	0.11	0.11
10	56.00	16.00	0.15	0.06	2.19	0.05	0.05
11	60.00	18.50	0.05	0.01	2.54	0.0	0.0
12	72.00	20.00	0.01	0.0	2.64	0.0	0.0
13	78.00	22.00	0.0	0.0	3.02	0.0	0.0

F = %PAN IN GREASE / ORIGINAL %PAN IN GREASE
Y = (%PAN - FINAL %PAN) / (ORIGINAL %PAN - FINAL %PAN

TABLE XVIII

SORPTION BY SILICA GREASE

(6 % CAB-O-SIL M-5 THICKENER--1 % PAN IN PERMEATING OIL)

SAMPLE NO	TIME (HOUR)	TOTAL VOL EXIT OIL (C C)	% ADDITIVE IN EXIT OIL	% ADDITIVE IN GREASE	V.EXIT.OIL / VOL.GREASE	F	Z
1	13.00	1.75	0.0	0.19	0.23	0.16	0.84
2	20.50	3.45	0.02	0.40	0.45	0.33	0.67
3	25.90	5.65	0.07	0.65	0.74	0.55	0.45
4	35.90	8.15	0.26	0.89	1.07	0.75	0.25
5	41.20	9.65	0.46	1.00	1.27	0.85	0.15
6	48.00	11.65	0.69	1.11	1.53	0.93	0.07
7	60.90	14.25	0.90	1.18	1.87	0.99	0.01
8	67.90	15.50	0.95	1.19	2.04	1.00	0.00
9	74.50	17.10	0.99	1.19	2.25	1.00	0.0
10	83.00	18.70	1.00	1.19	2.46	1.00	0.0

F = %PAN IN GREASE / FINAL %PAN IN GREASE

Z = 1 - (%PAN IN GREASE / FINAL %PAN IN GREASE)

TABLE XIX

EXTRACTION AFTER SORPTION

(6 % CAB-O-SIL M-5 THICKENER--1.19 % PAN IN GREASE)

SAMPLE NO	TIME (HOUR)	TOTAL VOL EXIT OIL (C C)	% ADDITIVE IN EXIT OIL	% ADDITIVE IN GREASE	V.EXIT.OIL / VOL.GREASE	# F	# Y
1	0.0	0.0	1.19	1.19	0.0	1.00	1.00
2	7.00	1.15	1.00	1.04	0.16	0.87	0.86
3	17.50	3.65	0.96	0.76	0.49	0.63	0.59
4	22.50	4.95	0.88	0.63	0.67	0.53	0.47
5	30.00	6.80	0.72	0.47	0.92	0.39	0.32
6	42.15	9.60	0.41	0.29	1.30	0.24	0.15
7	49.50	11.05	0.24	0.22	1.49	0.18	0.09
8	54.55	12.25	0.09	0.18	1.66	0.15	0.05
9	66.15	15.25	0.0	0.13	2.06	0.11	0.0
10	74.05	17.05	0.0	0.13	2.39	0.11	0.0

F = %PAN IN GREASE / ORIGINAL %PAN IN GREASE
Y = (%PAN - FINAL %PAN)/(ORIGINAL %PAN - FINAL %PAN)

TABLE XX

SORPTION BY SILICA GREASE

(6 % CAB-O-SIL H-5 THICKENER--0.25 % PAN IN PERMEATING OIL)

SAMPLE NO	TIME (HOUR)	TOTAL VOL EXIT OIL (C.C)	% ADDITIVE IN EXIT OIL	% ADDITIVE IN GREASE	V.EXIT.OIL / VOL.GREASE	F	Z
1	3.90	1.30	0.0	0.04	0.18	0.10	0.90
2	18.50	4.90	0.01	0.15	0.67	0.37	0.63
3	22.90	6.10	0.02	0.18	0.84	0.45	0.55
4	27.35	7.50	0.03	0.22	1.03	0.55	0.45
5	31.35	8.70	0.05	0.25	1.19	0.63	0.37
6	42.50	11.80	0.12	0.32	1.62	0.80	0.20
7	47.80	13.30	0.16	0.34	1.82	0.85	0.15
8	55.35	14.70	0.18	0.35	2.00	0.90	0.10
9	66.50	17.70	0.22	0.38	2.45	0.95	0.05
10	72.50	19.50	0.23	0.39	2.67	0.98	0.02
11	79.00	21.50	0.24	0.40	2.96	1.00	0.0
12	89.35	24.90	0.25	0.40	3.43	1.00	0.0

F = %PAN IN GREASE / FINAL %PAN IN GREASE
Z = 1 - (%PAN IN GREASE / FINAL %PAN IN GREASE)

TABLE XXI

SORPTION BY SILICA GREASE

(6 % CAB-O-SIL H-5 THICKENER--0.5 % PAN IN PERMEATING OIL)

SAMPLE NO	TIME (HOUR)	TOTAL VOL EXIT OIL (C.C)	% ADDITIVE IN EXIT OIL	% ADDITIVE IN GREASE	V.EXIT.OIL / VOL.GREASE	F	Z
1	7.40	1.45	0.01	0.11	0.23	0.15	0.85
2	11.45	3.00	0.05	0.21	0.48	0.28	0.72
3	23.00	6.60	0.16	0.41	1.05	0.55	0.45
4	26.10	8.50	0.24	0.49	1.36	0.66	0.34
5	30.10	11.60	0.32	0.60	1.85	0.80	0.20
6	34.50	14.90	0.36	0.67	2.38	0.90	0.10
7	46.00	20.90	0.46	0.74	3.33	0.99	0.01
8	52.10	23.40	0.52	0.75	3.97	1.00	0.0

F = %PAN IN GREASE / FINAL %PAN IN GREASE
Z = 1 - (%PAN IN GREASE / FINAL %PAN IN GREASE)

TABLE XXII

SORPTION BY SILICA GREASE

(6 % CAB-O-SIL H-5 THICKENER--1 % PAN IN PERMEATING OIL)

SAMPLE NO	TIME (HOUR)	TOTAL VOL EXIT OIL (C.C)	% ADDITIVE IN EXIT OIL	% ADDITIVE IN GREASE	V.EXIT.OIL / VOL.GREASE	# F	# Z
1	3.00	0.65	0.02	0.09	0.09	0.07	0.93
2	5.00	1.50	0.03	0.20	0.20	0.15	0.85
3	8.00	2.40	0.03	0.31	0.32	0.24	0.76
4	15.10	4.50	0.05	0.54	0.61	0.41	0.59
5	18.25	6.00	0.17	0.68	0.81	0.53	0.47
6	21.40	6.65	0.20	0.74	0.90	0.57	0.43
7	25.30	7.90	0.27	0.84	1.07	0.65	0.35
8	28.55	9.05	0.37	0.93	1.22	0.71	0.29
9	38.25	11.65	0.63	1.08	1.57	0.83	0.17
10	42.55	13.00	0.73	1.15	1.76	0.88	0.12
11	47.75	14.35	0.88	1.20	1.94	0.92	0.08
12	53.55	17.00	0.92	1.27	2.30	0.98	0.02
13	63.55	19.80	0.95	1.30	2.68	1.00	0.0
14	71.45	22.50	1.00	1.30	3.04	1.00	0.0

F = %PAN IN GREASE / FINAL %PAN IN GREASE
Z = 1 - (%PAN IN GREASE / FINAL %PAN IN GREASE)

TABLE XXIII

EXTRACTION AFTER SORPTION

(6 % CAB-O-SIL H-5 THICKENER--1.30 % PAN IN GREASE)

SAMPLE NO	TIME (HOUR)	TOTAL VOL EXIT OIL (C.C)	% ADDITIVE IN EXIT OIL	% ADDITIVE IN GREASE	#V.EXIT.OIL / VOL.GREASE#	# F	# Y
1	0.0	0.0	1.30	1.30	0.0	1.00	1.00
2	4.90	1.20	1.00	1.15	0.16	0.89	0.87
3	8.50	2.10	0.95	1.05	0.28	0.81	0.78
4	13.80	2.70	0.93	0.98	0.36	0.75	0.72
5	19.00	3.50	0.90	0.89	0.47	0.69	0.64
6	25.20	4.80	0.86	0.76	0.64	0.58	0.53
7	29.70	5.70	0.80	0.67	0.76	0.52	0.45
8	32.10	6.50	0.78	0.60	0.87	0.46	0.39
9	37.50	7.90	0.67	0.48	1.05	0.37	0.29
10	41.00	8.60	0.60	0.43	1.15	0.33	0.24
11	45.00	9.60	0.50	0.36	1.28	0.28	0.18
12	48.40	10.60	0.40	0.31	1.41	0.23	0.13
13	56.30	12.00	0.30	0.24	1.60	0.18	0.07
14	72.20	14.00	0.15	0.17	1.87	0.13	0.02
15	80.50	15.50	0.05	0.15	2.07	0.12	0.0
16	85.00	16.50	0.0	0.15	2.20	0.12	0.0

F = %PAN IN GREASE / ORIGINAL %PAN IN GREASE

Y = (%PAN - FINAL %PAN)/(ORIGINAL %PAN - FINAL %PAN)

TABLE XXIV

SORPTION BY SILICA GREASE

(6 % CAB-O-SIL H-5 THICKENER--2 % PAN IN PERMEATING OIL)

SAMPLE NO	TIME (HOUR)	TOTAL VOL EXIT OIL (C C)	% ADDITIVE IN EXIT OIL	% ADDITIVE IN GREASE	V.EXIT.OIL / VOL.GREASE	# F	# Z
1	5.10	1.20	0.0	0.34	0.16	0.14	0.86
2	9.45	2.70	0.0	0.74	0.37	0.30	0.70
3	15.40	4.10	0.04	1.07	0.56	0.43	0.57
4	18.30	5.00	0.09	1.27	0.68	0.52	0.48
5	23.10	6.10	0.20	1.50	0.83	0.61	0.39
6	29.40	7.90	0.48	1.82	1.08	0.74	0.26
7	32.00	8.50	0.70	1.91	1.16	0.77	0.23
8	34.50	9.40	0.97	2.04	1.28	0.83	0.17
9	41.40	10.80	1.32	2.21	1.47	0.89	0.11
10	46.50	12.40	1.63	2.35	1.69	0.95	0.05
11	52.10	13.95	1.84	2.43	1.90	0.99	0.01
12	53.00	14.00	1.88	2.44	1.91	0.99	0.01
13	58.20	15.80	1.98	2.47	2.16	1.00	0.0
14	65.10	17.20	2.00	2.47	2.35	1.00	0.0

F = %PAN IN GREASE / FINAL % PAN IN GREASE
Z = 1 - (%PAN IN GREASE / FINAL %PAN IN GREASE)

TABLE XXV

EXTRACTION AFTER SORPTION

(6 % CAB-O-SIL H-5 THICKENER--2.47 % PAN IN GREASE)

SAMPLE NO	TIME (HOUR)	TOTAL VOL EXIT OIL (C C)	% ADDITIVE IN EXIT OIL	% ADDITIVE IN GREASE	V.EXIT.OIL / VOL.GREASE	# F	# Y
1	0.0	0.0	2.47	2.47	0.0	1.00	1.00
2	9.00	2.00	1.90	1.99	0.26	0.80	0.80
3	18.00	3.90	1.80	1.57	0.51	0.64	0.63
4	25.00	5.50	1.70	1.26	0.72	0.51	0.50
5	31.40	7.20	1.60	0.97	0.95	0.39	0.37
6	40.50	9.00	1.30	0.70	1.18	0.28	0.26
7	45.00	10.30	0.91	0.53	1.36	0.22	0.19
8	52.50	12.00	0.62	0.35	1.58	0.14	0.12
9	56.30	13.10	0.46	0.26	1.72	0.11	0.08
10	67.00	16.00	0.12	0.10	2.11	0.04	0.01
11	72.00	17.50	0.03	0.07	2.30	0.03	0.0
12	81.10	19.60	0.0	0.07	2.58	0.03	0.0

F = %PAN IN GREASE / ORIGINAL %PAN IN GREASE

Y = (%PAN - FINAL %PAN)/(ORIGINAL %PAN - FINAL %PAN)

TABLE XXVI

SORPTION BY SILICA GREASE

(6 % CAB-O-SIL H-5 THICKENER--3 % PAN IN PERMEATING OIL)

SAMPLE NO	TIME (HOUR)	TOTAL VOL EXIT OIL (C C)	% ADDITIVE IN EXIT OIL	% ADDITIVE IN GREASE	V. EXIT.OIL / VOL.GREASE	# F	# Z
1	8.00	2.40	0.0	1.06	0.32	0.29	0.71
2	11.50	3.40	0.01	1.44	0.45	0.40	0.60
3	16.50	4.80	0.04	1.93	0.63	0.54	0.46
4	22.55	6.40	0.24	2.40	0.85	0.67	0.33
5	28.15	7.90	0.79	2.77	1.04	0.77	0.23
6	31.40	8.90	1.35	2.98	1.18	0.83	0.17
7	36.15	10.40	2.05	3.23	1.38	0.90	0.10
8	43.00	12.00	2.50	3.43	1.59	0.95	0.05
9	46.55	13.15	2.76	3.52	1.74	0.98	0.02
10	50.40	14.35	2.90	3.58	1.90	1.00	0.00
11	55.10	15.55	2.96	3.59	2.06	1.00	0.0
12	59.00	16.80	3.00	3.59	2.22	1.00	0.0

F = %PAN IN GREASE / FINAL %PAN IN GREASE
Z = 1 - (%PAN IN GREASE / FINAL %PAN IN GREASE)

TABLE XXVII

EXTRACTION AFTER SORPTION

(6 % CAB-O-SIL H-5 THICKENER--3.59 % PAN IN GREASE)

SAMPLE NO	TIME (HOUR)	TOTAL VOL EXIT OIL (C C)	% ADDITIVE IN EXIT OIL	% ADDITIVE IN GREASE	V.EXIT.OIL / VOL.GREASE	# F	# Y
1	0.0	0.0	3.59	3.59	0.0	1.00	1.00
2	3.00	0.75	3.00	3.29	0.10	0.92	0.91
3	8.30	2.30	3.00	2.69	0.31	0.75	0.73
4	12.40	3.50	2.90	2.26	0.47	0.63	0.61
5	19.00	6.30	2.70	1.37	0.84	0.38	0.35
6	26.15	8.10	2.00	0.93	1.08	0.26	0.22
7	30.55	9.40	1.00	0.68	1.25	0.19	0.14
8	41.55	12.45	0.46	0.31	1.66	0.09	0.03
9	48.10	14.25	0.20	0.22	1.90	0.06	0.01
10	51.40	15.40	0.10	0.20	2.05	0.06	0.0
11	55.00	16.40	0.07	0.20	2.19	0.06	0.0
12	67.25	19.70	0.03	0.20	2.63	0.06	0.0
13	71.10	20.80	0.0	0.20	2.77	0.06	0.0

F = %PAN IN GREASE / ORIGINAL %PAN IN GREASE
Y = (%PAN - FINAL %PAN)/(ORIGINAL %PAN - FINAL %PAN)

TABLE XXVIII

SORPTION BY SILICA GREASE

(6 % AEROSIL UNCOMPRESSED THICKENER--1 % PAN IN PERMEATING OIL)

SAMPLE NO	TIME (HOUR)	TOTAL VOL EXIT OIL (C C)	% ADDITIVE IN EXIT OIL	% ADDITIVE IN GREASE	# V. EXIT. OIL / VOL. GREASE #	# F	# Z
1	4.50	1.45	0.05	0.18	0.19	0.15	0.85
2	16.90	4.15	0.10	0.48	0.53	0.40	0.60
3	21.30	5.30	0.13	0.59	0.68	0.50	0.50
4	29.20	7.60	0.25	0.78	0.97	0.66	0.34
5	40.50	11.05	0.53	1.00	1.42	0.84	0.16
6	44.90	12.35	0.67	1.06	1.58	0.89	0.11
7	49.00	13.25	0.75	1.10	1.70	0.92	0.08
8	54.00	14.25	0.84	1.13	1.83	0.95	0.05
9	65.30	17.45	0.97	1.19	2.24	1.00	0.00
10	68.30	18.35	0.99	1.19	2.35	1.00	0.0
11	73.00	19.75	1.00	1.19	2.53	1.00	0.0

F= %PAN IN GREASE / FINAL %PAN IN GREASE
Z = 1 - (%PAN IN GREASE / FINAL %PAN IN GREASE)

TABLE XXIX

EXTRACTION AFTER SORPTION

(6 % AEROSIL UNCOMPRESSED THICKENER--1.19 % PAN IN GREASE)

SAMPLE NO	TIME (HOUR)	TOTAL VOL EXIT OIL (C.C)	% ADDITIVE IN EXIT OIL	% ADDITIVE IN GREASE	V.EXIT.OIL / VOL.GREASE	F	Y
1	0.0	0.0	1.19	1.19	0.0	1.00	1.00
2	4.40	1.45	0.95	1.03	0.19	0.86	0.86
3	8.20	2.55	0.85	0.91	0.33	0.76	0.77
4	13.30	4.05	0.81	0.76	0.52	0.64	0.64
5	25.10	6.55	0.75	0.54	0.84	0.45	0.46
6	31.55	8.32	0.68	0.40	1.07	0.34	0.34
7	37.20	10.07	0.60	0.29	1.29	0.24	0.25
8	48.15	13.50	0.32	0.11	1.73	0.09	0.10
9	56.10	15.45	0.13	0.05	1.98	0.04	0.05
10	71.55	18.27	0.01	0.01	2.34	0.02	0.0
11	80.15	19.77	0.0	0.01	2.53	0.01	0.0
12	96.45	20.57	0.0	0.0	2.64	0.01	0.0

F = %PAN IN GREASE / ORIGINAL %PAN IN GREASE
Y = (%PAN - FINAL %PAN)/(ORIGINAL %PAN - FINAL %PAN)

TABLE XXX

SORPTION BY SILICA GREASE

(6 % AEROSIL 2491 THICKENER--1 % PAN IN PERMEATING OIL)

SAMPLE NO	TIME (HOUR)	TOTAL VOL EXIT OIL (C C)	% ADDITIVE IN EXIT OIL	% ADDITIVE IN GREASE	V.EXIT.OIL # ---------- # VOL.GREASE	# F	# Z
1	9.00	2.10	0.0	0.33	0.29	0.27	0.73
2	20.00	4.60	0.0	0.65	0.63	0.53	0.47
3	25.40	6.00	0.09	0.80	0.82	0.65	0.35
4	29.50	7.20	0.24	0.90	0.98	0.74	0.26
5	33.90	8.10	0.38	0.97	1.11	0.79	0.21
6	39.40	9.50	0.57	1.06	1.30	0.86	0.14
7	45.00	10.90	0.77	1.13	1.49	0.92	0.08
8	51.20	12.45	0.92	1.18	1.70	0.96	0.04
9	57.30	14.20	0.98	1.21	1.94	0.99	0.01
10	67.90	16.60	1.00	1.22	2.27	1.00	0.0
11	72.90	17.80	1.00	1.22	2.44	1.00	0.0

F = %PAN IN GREASE / FINAL %PAN IN GREASE
Z = 1 - (%PAN IN GREASE / FINAL %PAN IN GREASE)

TABLE XXXI

EXTRACTION AFTER SORPTION

(6 % AEROSIL 2491 THICKENER--1.22 % PAN IN GREASE)

SAMPLE NO	TIME (HOUR)	TOTAL VOL EXIT OIL (C.C)	% ADDITIVE IN EXIT OIL	% ADDITIVE IN GREASE	#V.EXIT.OIL / VOL.GREASE#	# F	# Y
1	0.0	0.0	1.22	1.22	0.0	1.00	1.00
2	7.00	1.50	1.00	1.02	0.21	0.84	0.83
3	11.45	2.60	1.00	0.89	0.36	0.73	0.71
4	22.45	5.05	1.00	0.62	0.69	0.51	0.49
5	27.45	6.40	0.80	0.50	0.88	0.41	0.38
6	31.45	7.40	0.66	0.41	1.01	0.34	0.31
7	36.30	8.65	0.56	0.32	1.18	0.26	0.23
8	46.45	11.30	0.27	0.17	1.55	0.14	0.10
9	52.15	12.80	0.12	0.11	1.75	0.09	0.05
10	59.15	14.45	0.01	0.07	1.98	0.06	0.01
11	69.15	16.80	0.0	0.06	2.30	0.05	0.0
12	72.55	17.70	0.0	0.06	2.42	0.05	0.0

F = %PAN IN GREASE / ORIGINAL %PAN IN GREASE
Y = (%PAN - FINAL %PAN)/(ORIGINAL %PAN - FINAL %PAN)

TABLE XXXII

SORPTION BY SILICA GREASE

(6 % AEROSIL 2491-380 THICKENER--1 % PAN IN PERMEATING OIL)

SAMPLE NO	TIME (HOUR)	TOTAL VOL EXIT OIL (C C)	% ADDITIVE IN EXIT OIL	% ADDITIVE IN GREASE	# V.EXIT.OIL / VOL.GREASE #	# F	# Z
1	19.50	1.10	0.0	0.16	0.16	0.14	0.86
2	25.30	1.90	0.0	0.28	0.27	0.23	0.77
3	34.00	2.90	0.01	0.41	0.41	0.34	0.66
4	39.50	3.30	0.02	0.52	0.54	0.43	0.57
5	46.20	4.70	0.05	0.62	0.67	0.51	0.49
6	59.70	6.20	0.10	0.77	0.88	0.63	0.37
7	75.20	7.80	0.37	0.90	1.11	0.75	0.25
8	94.20	9.60	0.61	1.03	1.37	0.85	0.15
9	108.20	11.20	0.76	1.11	1.60	0.92	0.08
10	115.00	12.20	0.77	1.15	1.74	0.95	0.05
11	119.80	13.00	0.87	1.17	1.85	0.97	0.03
12	131.20	14.50	0.92	1.20	2.07	1.00	0.0
13	146.80	15.00	0.93	1.21	2.14	1.00	0.0
14	150.40	17.50	1.00	1.22	2.50	1.00	0.0

F = %PAN IN GREASE / FINAL %PAN IN GREASE
Z = 1 - (%PAN IN GREASE / FINAL %PAN IN GREASE)

TABLE XXXIII

EXTRACTION AFTER SORPTION

(6 % AEROSIL 2491-380 THICKENER--1.22 % PAN IN GREASE)

SAMPLE NO	TIME (HOUR)	TOTAL VOL EXIT OIL (C C)	% ADDITIVE IN EXIT OIL	% ADDITIVE IN GREASE	V.EXIT.OIL / VOL.GREASE	# F	# Y
1	0.0	0.0	1.22	1.22	0.0	1.00	1.00
2	7.00	1.60	0.95	1.02	0.22	0.83	0.83
3	11.50	2.50	0.94	0.91	0.34	0.75	0.74
4	22.50	4.80	0.89	0.66	0.65	0.54	0.53
5	27.50	6.00	0.86	0.55	0.82	0.45	0.43
6	31.50	6.90	0.78	0.47	0.94	0.38	0.36
7	36.50	8.00	0.70	0.38	1.09	0.31	0.29
8	46.50	10.40	0.45	0.22	1.41	0.18	0.15
9	52.20	11.70	0.25	0.15	1.59	0.12	0.10
10	59.20	13.15	0.15	0.09	1.79	0.08	0.05
11	69.20	15.25	0.01	0.05	2.07	0.04	0.01
12	72.50	16.25	0.0	0.04	2.21	0.03	0.0
13	78.00	18.50	0.0	0.04	2.52	0.03	0.0

F = %PAN IN GREASE / ORIGINAL %PAN IN GREASE
Y = (%PAN - FINAL %PAN)/(ORIGINAL %PAN - FINAL %PAN)

TABLE XXXIV

SORPTION BY SILICA GREASE

(6 % AEROSIL MOX-170 THICKENER--1 % PAN IN PERMEATING OIL)

SAMPLE NO	TIME (HOUR)	TOTAL VOL EXIT OIL (C C)	% ADDITIVE IN EXIT OIL	% ADDITIVE IN GREASE	V.EXIT.OIL ---------- VOL.GREASE	# F	# Z
1	6.00	2.10	0.0	0.29	0.29	0.25	0.75
2	11.05	4.00	0.11	0.52	0.56	0.43	0.57
3	16.30	6.25	0.32	0.73	0.87	0.61	0.39
4	19.50	7.75	0.41	0.85	1.08	0.71	0.29
5	24.30	9.95	0.61	0.99	1.38	0.83	0.17
6	36.50	15.45	0.86	1.17	2.15	0.98	0.02
7	39.20	16.85	0.94	1.19	2.34	1.00	0.00
8	41.80	18.25	1.00	1.19	2.53	1.00	0.0

F = %PAN IN GREASE / FINAL %PAN IN GREASE

Z = 1 - (%PAN IN GREASE / FINAL %PAN IN GREASE)

TABLE XXXV

EXTRACTION AFTER SORPTION

(6 % AEROSIL MOX-170 THICKENER--1.19 % PAN IN GREASE)

SAMPLE NO	TIME (HOUR)	TOTAL VOL EXIT OIL (C.C)	% ADDITIVE IN EXIT OIL	% ADDITIVE IN GREASE	V. EXIT. OIL / VOL. GREASE	F	Y
1	0.0	0.0	1.19	1.19	0.0	1.00	1.00
2	3.15	1.50	0.93	0.99	0.22	0.83	0.82
3	4.50	2.40	0.92	0.88	0.35	0.74	0.72
4	9.40	4.60	0.80	0.65	0.67	0.55	0.51
5	12.50	6.20	0.69	0.51	0.91	0.43	0.38
6	15.25	7.55	0.52	0.41	1.10	0.34	0.29
7	21.40	10.00	0.40	0.26	1.46	0.22	0.16
8	25.10	11.10	0.25	0.21	1.62	0.18	0.11
9	30.05	12.60	0.20	0.16	1.84	0.13	0.06
10	36.10	14.05	0.09	0.12	2.05	0.10	0.03
11	39.04	15.55	0.05	0.10	2.27	0.08	0.01
12	46.48	17.15	0.03	0.09	2.51	0.07	0.0
13	48.48	18.55	0.0	0.09	2.71	0.07	0.0

F = %PAN IN GREASE / ORIGINAL %PAN IN GREASE
Y = (%PAN - FINAL %PAN)/(ORIGINAL %PAN - FINAL %PAN)

TABLE XXXVI

SORPTION BY GREASE

(6 % ALUMINUM OXIDE THICKENER--1 % PAN IN PERMEATING OIL)

SAMPLE NO	TIME (HOUR)	TOTAL VOL EXIT OIL (C C)	% ADDITIVE IN EXIT OIL	% ADDITIVE IN GREASE	#V.EXIT.OIL / VOL.GREASE#	# F	# Z
1	4.20	1.60	0.05	0.17	0.21	0.16	0.84
2	8.00	3.25	0.37	0.32	0.42	0.31	0.69
3	14.20	5.55	0.45	0.50	0.73	0.49	0.51
4	18.40	7.10	0.51	0.60	0.93	0.59	0.41
5	24.30	9.05	0.58	0.71	1.18	0.69	0.31
6	28.20	10.75	0.64	0.78	1.41	0.77	0.23
7	32.30	12.80	0.70	0.86	1.67	0.84	0.16
8	42.20	16.30	0.83	0.94	2.13	0.93	0.07
9	45.45	17.60	0.87	0.96	2.30	0.95	0.05
10	51.50	19.60	0.91	0.99	2.56	0.97	0.03
11	58.50	22.20	0.95	1.01	2.90	0.99	0.01
12	66.30	25.00	1.00	1.02	3.27	1.00	0.0

F = %PAN IN GREASE / FINAL %PAN IN GREASE
Z = 1 - (%PAN IN GREASE / FINAL %PAN IN GREASE)

TABLE XXXVII

EXTRACTION AFTER SORPTION

(6 % ALUMINUM OXIDE THICKENER--1.02 % PAN IN GREASE)

SAMPLE NO	TIME (HOUR)	TOTAL VOL EXIT OIL (C C)	% ADDITIVE IN EXIT OIL	% ADDITIVE IN GREASE	V.EXIT.OIL / VOL.GREASE	F	Y
1	0.0	0.0	1.02	1.02	0.0	1.00	1.00
2	10.50	4.00	0.58	0.65	0.50	0.64	0.65
3	19.05	7.80	0.54	0.40	0.98	0.39	0.41
4	22.50	10.20	0.37	0.27	1.28	0.27	0.29
5	32.40	14.40	0.25	0.12	1.81	0.12	0.15
6	39.10	16.90	0.23	0.06	2.13	0.06	0.09
7	44.10	19.50	0.14	0.02	2.45	0.02	0.05
8	48.50	21.10	0.06	-0.00	2.65	-0.00	0.03
9	59.10	25.00	0.04	-0.03	3.14	-0.03	0.01
10	67.20	28.30	0.00	-0.03	3.56	-0.03	0.00
11	71.50	30.40	0.0	-0.04	3.82	-0.03	0.0

F = %PAN IN GREASE / ORIGINAL %PAN IN GREASE
Y = (%PAN - FINAL %PAN)/(ORIGINAL %PAN - FINAL %PAN)

TABLE XXXVIII

SORPTION BY HALF THICKNESS SILICA GREASE

(6 % CAB-O-SIL H-5 THICKENER--1 % PAN IN PERMEATING OIL)

SAMPLE NO	TIME (HOUR)	TOTAL VOL EXIT OIL (C C)	% ADDITIVE IN EXIT OIL	% ADDITIVE IN GREASE	# V.EXIT.OIL / VOL.GREASE #	# F	# Z
1	0.0	0.0	0.0	0.0	0.0	0.0	1.00
2	2.25	1.20	0.0	0.29	0.31	0.20	0.80
3	5.50	2.50	0.05	0.60	0.65	0.43	0.57
4	7.90	4.00	0.12	0.92	1.03	0.65	0.35
5	16.25	5.60	0.29	1.18	1.45	0.83	0.17
6	19.30	6.80	0.80	1.30	1.76	0.92	0.08
7	23.30	8.40	0.92	1.39	2.17	0.98	0.02
8	28.30	10.60	0.95	1.42	2.74	1.00	0.0
9	38.60	13.70	0.98	1.42	3.54	1.00	0.0
10	42.90	14.90	1.00	1.42	3.85	1.00	0.0

F = %PAN IN GREASE / FINAL %PAN IN GREASE
Z = 1 - (%PAN IN GREASE / FINAL %PAN IN GREASE)

TABLE XXXIX

EXTRACTION AFTER SORPTION BY HALF THICKNESS SILICA GREASE

(6 % CAB-O-SIL H-5 THICKENER--1.42 % PAN IN GREASE)

SAMPLE NO	TIME (HOUR)	TOTAL VOL EXIT OIL (C C)	% ADDITIVE IN EXIT OIL	% ADDITIVE IN GREASE	V.EXIT.OIL / VOL.GREASE	F	Y
1	0.0	0.0	1.42	1.42	0.0	1.00	1.00
2	3.50	1.00	1.00	1.17	0.26	0.82	0.80
3	7.50	2.15	0.92	0.97	0.56	0.65	0.61
4	11.10	3.10	0.88	0.74	0.80	0.52	0.48
5	16.00	4.00	0.80	0.61	1.03	0.43	0.37
6	22.45	5.80	0.40	0.39	1.50	0.28	0.20
7	28.05	7.00	0.20	0.29	1.81	0.21	0.13
8	31.45	7.90	0.13	0.24	2.04	0.17	0.08
9	36.15	9.10	0.08	0.18	2.35	0.13	0.04
10	30.10	10.00	0.07	0.16	2.58	0.11	0.02
11	47.00	11.45	0.05	0.13	2.96	0.09	0.00
12	51.20	12.45	0.03	0.13	3.22	0.09	0.0
13	55.15	13.55	0.02	0.13	3.50	0.09	0.0
14	59.00	14.65	0.01	0.13	3.79	0.09	0.0
15	65.10	16.00	0.0	0.13	4.13	0.09	0.0

F = %PAN IN GREASE / ORIGINAL %PAN IN GREASE
Y = (%PAN - FINAL %PAN)/(ORIGINAL %PAN - FINAL %PAN)

TABLE XXXX

SORPTION BY DOUBLE THICKNESS SILICA GREASE

(6 % CAB-O-SIL H-5 THICKENER--1 % PAN IN PERMEATING OIL)

SAMPLE NO	TIME (HOUR)	TOTAL VOL EXIT OIL (C.C)	% ADDITIVE IN EXIT OIL	% ADDITIVE IN GREASE	V. EXIT OIL / VOL. GREASE	F	Z
1	92.60	10.80	0.0	0.65	0.72	0.54	0.46
2	117.30	13.60	0.06	0.81	0.91	0.68	0.32
3	120.30	15.40	0.23	0.92	1.03	0.77	0.23
4	133.40	17.00	0.35	0.99	1.14	0.83	0.17
5	154.90	19.50	0.52	1.08	1.30	0.92	0.08
6	179.90	22.10	0.72	1.14	1.48	0.95	0.05
7	189.00	23.20	0.77	1.16	1.55	0.97	0.03
8	216.00	24.90	0.86	1.18	1.66	0.98	0.02
9	238.50	26.10	0.92	1.19	1.74	0.98	0.02
10	253.30	27.70	0.94	1.20	1.85	0.99	0.01
11	263.00	28.80	0.95	1.21	1.93	0.99	0.01
12	275.30	30.25	0.96	1.22	2.02	1.00	0.0
13	288.20	31.75	0.97	1.24	2.12	1.00	0.0
14	306.10	33.65	0.98	1.25	2.25	1.00	0.0
15	322.30	35.60	1.00	1.26	2.38	1.00	0.0

F = %PAN IN GREASE / FINAL %PAN IN GREASE

Z = 1 - (%PAN IN GREASE / FINAL %PAN IN GREASE)

TABLE XXXXI

EXTRACTION AFTER SORPTION BY DOUBLE THICKNESS SILICA GREASE
(6 % CAB-O-SIL H-5 THICKENER--1.26 % PAN IN GREASE)

SAMPLE NO	TIME (HOUR)	TOTAL VOL EXIT OIL (C.C)	% ADDITIVE IN EXIT OIL	% ADDITIVE IN GREASE	V.EXIT OIL / VOL.GREASE	F #	Y #
1	69.00	7.20	0.97	0.79	0.48	0.61	0.58
2	93.90	9.40	0.93	0.67	0.63	0.49	0.47
3	117.50	11.70	0.74	0.55	0.78	0.37	0.35
4	140.50	14.00	0.62	0.45	0.94	0.27	0.26
5	169.50	16.70	0.50	0.36	1.12	0.18	0.17
6	181.00	18.00	0.35	0.34	1.21	0.16	0.15
7	192.50	19.30	0.25	0.31	1.29	0.13	0.12
8	204.90	20.70	0.22	0.28	1.38	0.10	0.10
9	217.00	22.10	0.20	0.26	1.48	0.08	0.08
10	226.80	23.20	0.18	0.25	1.55	0.07	0.07
11	241.80	24.90	0.15	0.23	1.67	0.05	0.05
12	253.80	26.40	0.10	0.21	1.77	0.03	0.03
13	265.30	27.80	0.08	0.19	1.86	0.01	0.01
14	290.50	30.30	0.05	0.18	2.03	0.0	0.0
15	312.90	32.80	0.0	0.18	2.19	0.0	0.0

-F = %PAN IN GREASE / ORIGINAL % PAN IN GREASE
Y = (%PAN - FINAL %PAN)/(ORIGINAL %PAN - FINAL %PAN)

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IX. VITA

The author was born on June 11, 1938, in Taiwan, Republic of China. He received his primary and high school education in Hsinchu, his home town. After high school, he entered National Taiwan University, Taipei, Taiwan in September 1958 and received his B. S. degree in Chemical Engineering in June 1962. After graduation he served in the Republic of China Army one year and then was employed by Mobil-China Allied Chemical Industries LTD. until he came to the United States. The author enrolled in the Graduate School of University of Missouri at Rolla in September 1966.