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**BASIC FACTORS IN THE FORMATION AND STABILITY
OF NON-SOAP LUBRICATING GREASES**

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FOREWORD

This report was prepared by the Lehigh Institute of Research under USAF Contract No. AF 33(616)-3999. This contract was initiated under Project 3044, "Aviation Lubricants", Task No. 73310, "Aircraft Lubricating Greases". The work was administered under the direction of the Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, with Mr. Herbert Schwenker acting as project engineer.

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Rheological measurements of dispersions of grease thickeners in pure vehicles or in vehicles containing water, additives or both these components have been carried out. Previous studies were made with the systems Aerosil--Plexol 201 and Santocel C2-paraffin oil. These types of measurements have been extended to include both polar and nonpolar solids dispersed in grease vehicles. The solids studied now include Copper Phthalocyanine, G. S. Hydrophobic Silica, HiSil, Aerosil, Santocel and Permangel. It was demonstrated that surface hydrophilicity and the presence of trace water far overshadows the influence of particle diameter and shape in the formation of gel structure by solid thickeners.


Further studies of the behavior of commercial additives have been made by measuring the change in consistency of a grease with increased concentration of additive. Because of the very complex nature of additive behavior a fundamental program has been developed to learn more of this phenomenon. This study has begun and includes measurements of additive adsorption from solution by selected solids as well as heat of immersional wetting measurements of solids in additive solutions at various concentrations. Studies thus far indicate that the heat of solution of additive in the grease vehicle and the heat of wetting of the solid thickener by pure additive relative to the vehicle appear to govern adsorption from solution. With Aerosil, a weakly polar solid, the heats of solution of the additives studied appears to predominate, and only those additives which dislike the vehicle (high endothermic heats of solution) adsorb and fluidize Aerosil-built greases. With rutile-built greases, however, the surface polarity of the thickener and consequent heat of adsorption is sufficiently high to influence adsorption of additives ineffective in Aerosil-built greases.

The program for the preparation of arylurea thickened greases has progressed satisfactorily. Several variables have been found to influence the particle diameter of the thickener solid formed. These include type of reactant, method of addition of reactants and the temperature of the reaction. Trace or larger quantities of water drastically increase particle size of arylurea thickeners prepared in solvents from which they can be isolated. The effect on greases prepared "in situ" is believed to be similar. This point is being checked.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:


R. T. Schwartz
Chief Organic Materials Branch
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INTRODUCTION

The influence of selected additives on the consistencies of non-soap lubricating greases has been investigated. The large amount of qualitative data collected in the past and based on penetration measurements for the behavior of additives in grease systems is being augmented by more precise measurements of solution adsorption isotherms, heats of solution and heats of adsorption from solution onto thickener surfaces. These more precise data have made possible the recognition of the important parameters which govern additive action. Such data will allow the application of the quantitative theory to the behavior of additives in non-soap grease systems.

The study of the many variables which govern arylurea particle formation in grease vehicles has also continued. Emphasis has been shifted from the "in situ" method of arylurea preparation in solvents from which the thickener particles can be easily separated. Heats of immersionsal wetting and surface area measurements will be made to differentiate between the variety of preparative techniques employed.

Miscellaneous studies which include rheological measurements and a continuation of the literature review have been made also.

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I. ADDITIVE INFLUENCE ON NON-SOAP GREASES

Studies of the Behavior of Practical Additives. - The numerous studies of the influence of the heptyl additives and their benzene analogues have been reported earlier (1). Recently, such studies were continued using complex, practical additives. Penetration data versus wt.% additive for a HiSil-Plexol 201 grease system are shown plotted in Figures 1, 2 and 3. The results for several commercial additives are illustrated in Figure 1. NaSul BSN (di nonyl naphthalene sulfonates) was found to be as effective a thinning agent for this grease system as the heptyl alcohol and amine. The Agerite Stalite (oxylated and styrated diphenyl amines) and Agerite powder (phenyl beta naphthyl amine) had little effect on grease consistency. It has already been demonstrated that increasing the complexity of a good deflocculating agent such as a straight chain amine by the addition of phenyl or naphthyl groups decreases the ability of the agent to thin grease systems. The small influence of the Agerite compounds on grease consistency could well be a desirable property since these materials are used as oxidation inhibitors and adsorption onto the solid would, undoubtedly, reduce their inhibiting power. These compounds were supplied by the R. T. Vanderbilt Company, New York, N. Y.

Making an organic amine or alcohol more complex by lengthening the chain obviously does not have the same effect as the addition of aromatic groups. This is illustrated in Figure 2; Armac CD and Alrose Amine S, long chain organic hydroxy amines, are excellent deflocculating agents. Indeed, it was also shown (1) that films of these materials adsorbed on polar solids are more stable to displacement by water than the corresponding heptyl derivatives.

The glycols, as expected, are not effective deflocculating agents for polar solids dispersed in a nonpolar grease vehicle.

Fundamental Studies of Additive Action. - A greater insight into the exact role of additive action in non-soap grease systems is now being obtained through solution adsorption, heat of wetting and solubility measurements. Attention once again was focused on the influence of the heptyl additives in non-soap grease systems containing about 15 wt.% polar solids dispersed in Plexol 201 or paraffin oil prior to quantitative studies of complex additives. These heptyl additives included the amine, alcohol, acid, chloride and the aldehyde. The solids, in order of increasing surface polarity, were Aerosil, HiSil and rutile. The alcohol and amine in concentrations from 1 to 2 wt. % completely fluidized greases built with these solids. The acid, chloride and aldehyde had little influence on Aerosil-built greases; their influence, however, increased as the surface polarity of the thickener solid increased. For example, all the additives except the chloride fluidized rutile-built greases and at relatively low concentrations of from 1 to 3 wt.%.

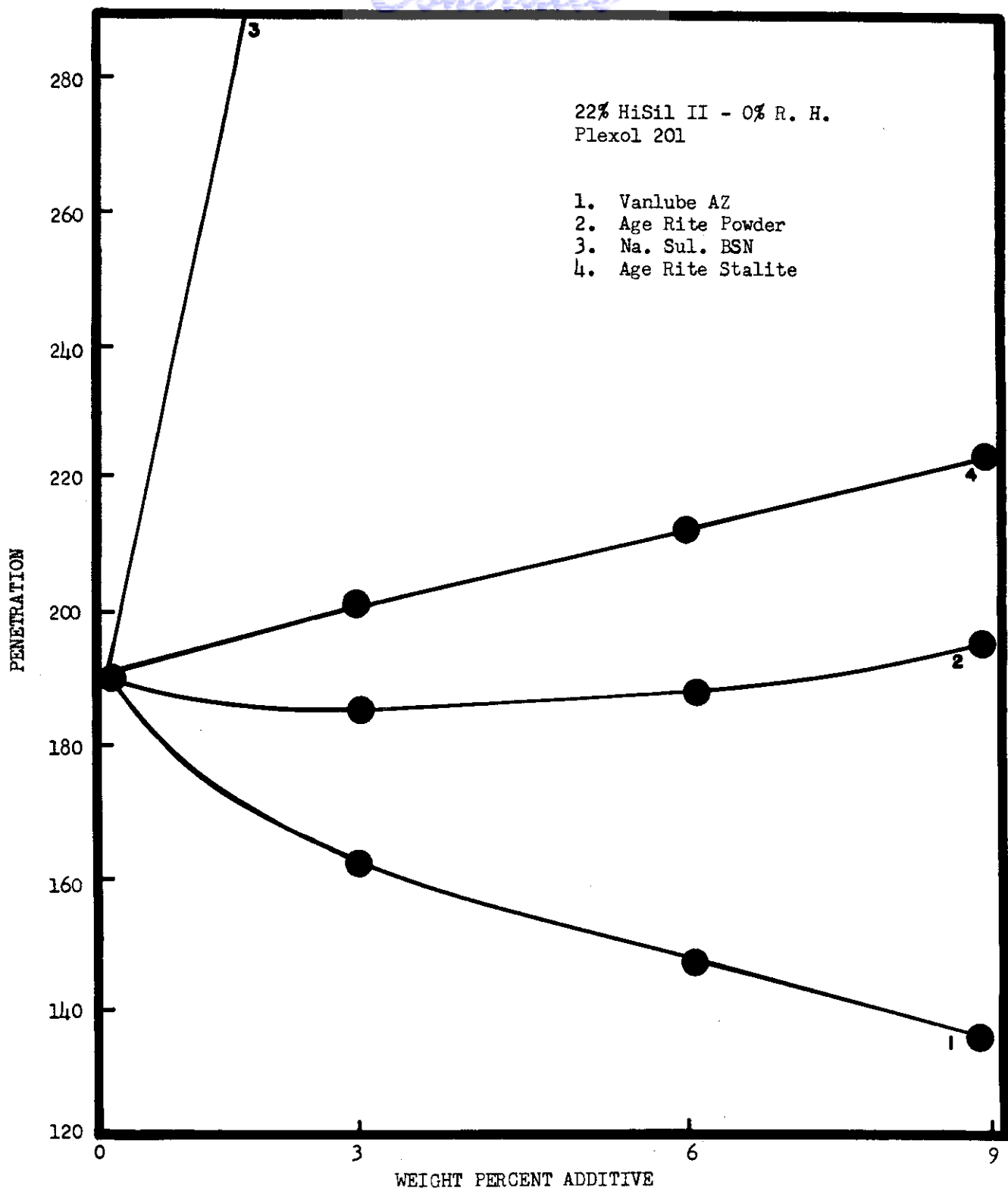


Figure 1. Influence of Commercial Additives on a HiSil - Plexol 201 Grease.

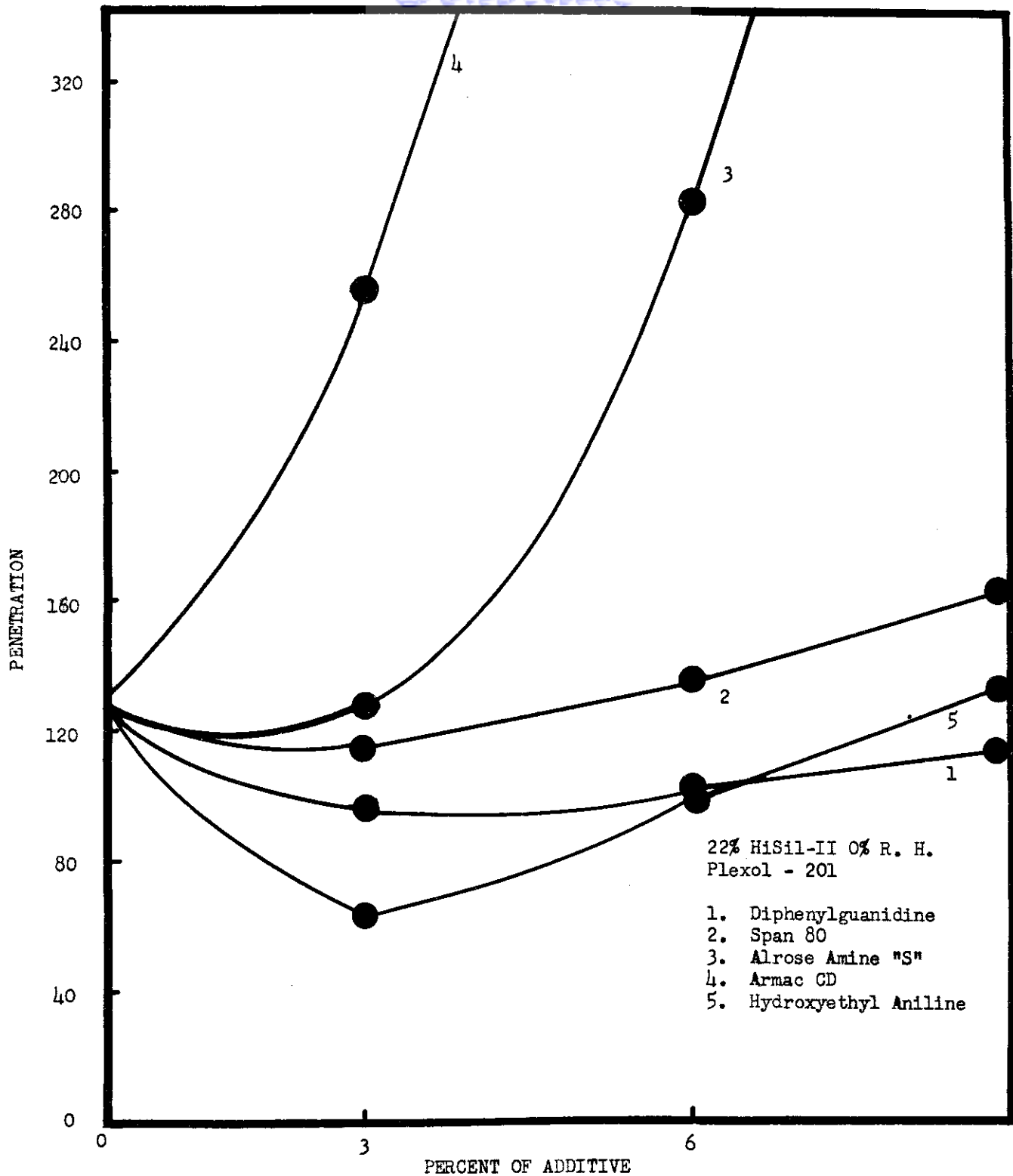


Figure 2. Influence of Basic Additives on a HiSil - Plexol 201 Grease.

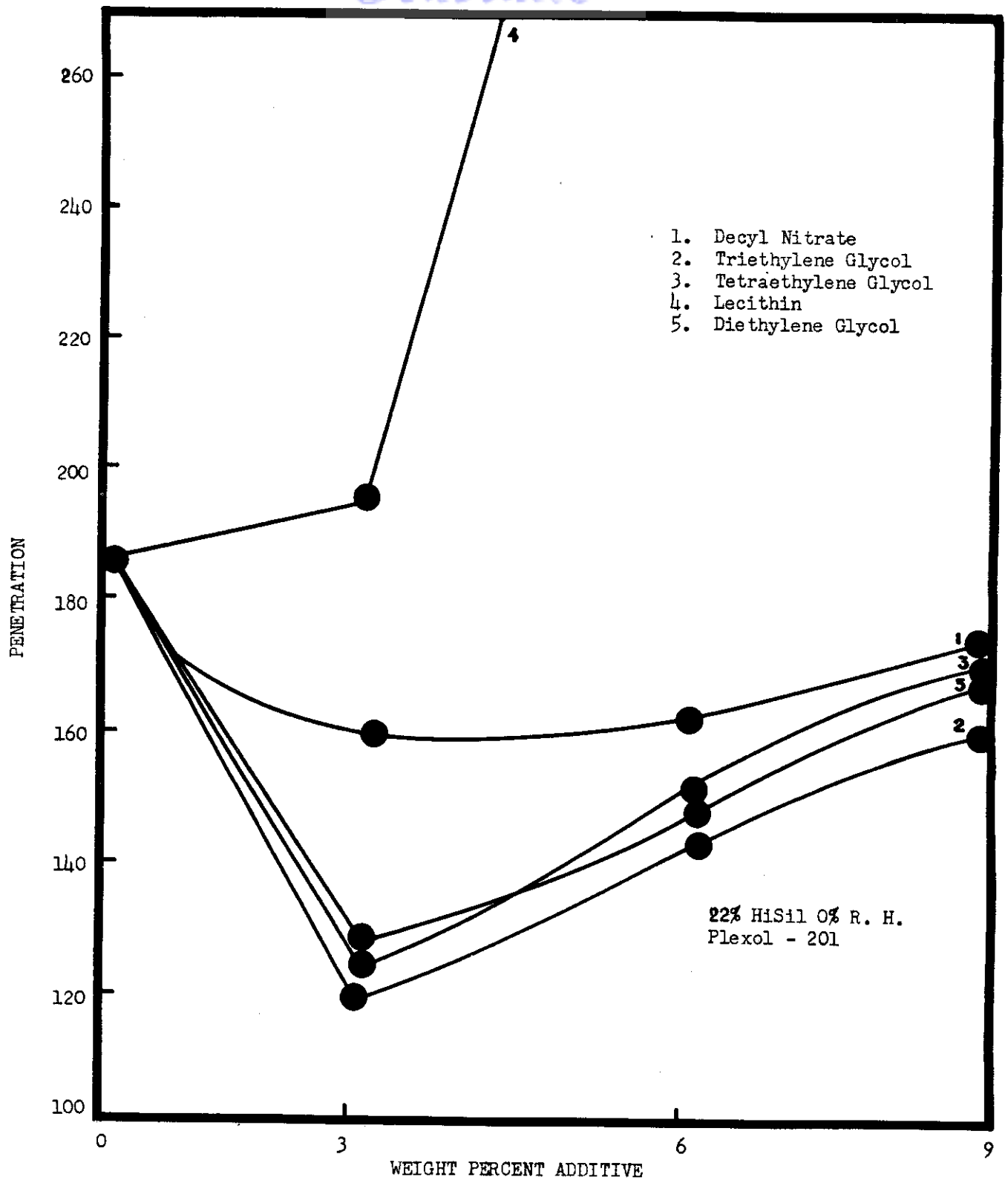


Figure 3. Influence of Nitrate, Glycol and Lecithin Additives on a HiSil - Plexol 201 Grease.

The grease thickeners were dried before dispersion but the vehicles were not, and undoubtedly contained small quantities of dissolved water. This dissolved water, it should be recalled, is important in giving structure to greases containing the polar solids at these concentrations. The marked thinning action of the amine and alcohol could have resulted from a preferential adsorption of these compounds from solution by the solid. The adsorbed organic film apparently sterically prevented the flocculation of particles by the trace water present in the system. Indeed, the drying agents MgSO_4 and P_2O_5 had the same effect on these systems. The increased influence of the additives as the surface polarity of the solid increased also suggested adsorption from solution as a prerequisite to fluidization.

Limited adsorption of the aldehyde, acid and chloride in the additive concentration studied could account for the small effects of these additives on Aerosil-nonpolar vehicle systems. Surprisingly, however, the acid and chloride were still without effect in this grease system at concentrations up to 12 wt. %. Measurements completed or now in progress should, however, provide the information necessary for an exact explanation of additive behavior just discussed.

Theoretical Considerations Concerning Adsorption From Solution. - When a solid is immersed in a solution some of the solute is adsorbed onto the solid surface. In the absence of preferential adsorption of the solute or at low solute concentrations solvent adsorption also occurs. The surface free energy of the solid is replaced by the surface free energies of the adsorbed solvent-solid and solute-solid interfaces. In addition free energy changes occur between these new adsorbed surfaces and the remaining solution. The total heat effects due to the immersion of a clean solid into a solution are the sum of the heat effects for these processes. In addition, a heat effect due to the dilution of the solution must be considered. The total heat of immersion is given by:

$$(1) \quad \Delta H_{\text{total}} = \sum \Delta H_{\text{immersion}} + \sum \Delta H_{\text{dilution}}$$

where $\sum \Delta H_{\text{immersion}}$ includes all heat effects due to adsorption or wetting and interfacial changes, and $\sum \Delta H_{\text{dilution}}$ includes heat effects due to removing solute from solution.

For a binary solution the heat effect due to concentration changes of the solution is given by the change in the heat of solution between the equilibrium and initial concentrations, i.e., $\Delta H_{\text{solution}}/\Delta C$. If the heat of solution is expressed in ergs per mole of solute then

$$(2) \quad \sum \Delta H_{\text{dilution}} = N_s \frac{\Delta h_{\text{solution}}}{\Delta C}$$

where N_s is the number of moles of solute adsorbed per unit area of solid.

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The term, $\sum \Delta H_{\text{immersion}}$, will generally be difficult to define. In a previous paper (2) an equation was developed to express the total heat evolved in terms of its component parts for the immersion of Graphon* in solutions of butanol in water.

The heat of immersion term, $\sum \Delta H_{\text{immersion}}$, will be a combination of three terms. The heat of adsorption of solute on a portion of the surface, $(h_{sL} - h_{sfL})$, the heat of wetting of the remainder of the surface by solvent, h_w , and a term for the wetting of the adsorbed solute surface, (h_I) . Thus the general equation 1 can be expanded to give

$$(3) \Delta H_{\text{total}} = -N_s \frac{\Delta h_{\text{soln.}}}{\Delta C} + (h_{sL} - h_{sfL}) + h_w + h_I.$$

Usually the total heat effect, ΔH_{total} , the heat of dilution term and the heat of wetting of that portion covered by the solvent molecules can be determined readily from experimental data. The heat due to interfacial changes, h_I , can be approximated with some degree of certainty. However, the heat of adsorption of the solute which represents the difference in the heat of immersion of the clean solid, h_{sL} , and a solid covered with N_s adsorbed molecules, h_{sfL} , cannot be obtained for many substances which are solids or liquids with very low vapor pressures. Indeed, equation 3 has been used successfully to calculate the heat of adsorption for the system Graphon-butanol-water (2).

Graphon presents a homogeneous surface for adsorption, thus it is reasonable to expect that the heat of adsorption would depend only on the amount of material being adsorbed. Furthermore, this surface is hydrophobic and is preferentially wet by n-butyl alcohol. The heat of adsorption of butanol may be expressed as the fraction of the surface covered by alcohol molecules, θ , times the total heat of adsorption at monolayer coverage $(h_{sL} - h_{se})$ which is $h_{sL} - h_{sfL} = \theta (h_{sL} - h_{se})$. Assuming that the heat of wetting of Graphon by water is constant, this heat effect may be expressed in terms of the fraction of surface covered by water molecules $(1 - \theta)$. Equation 3 then becomes

$$(4) \Delta H_{\text{total}} = -N_s \frac{\Delta h_{\text{soln.}}}{\Delta C} + \theta (h_{sL} - h_{se}) + (1 - \theta) h_{sL}^1 + \theta h_I$$

Application of this equation required solution adsorption isotherms, heat of immersion in solution and heat of solution as well as other experimental data.

* Graphon is a graphitized carbon black characterized by a homogeneous surface.

The assumptions used in developing equation 1 are specific for the system under consideration. Similar but more complex equations can be developed for other systems (heterogeneous or homopolar adsorbents, polar or nonpolar solutes and solvents, etc.). Considerable experimental data has been collected concerning additive influence on non-soap grease systems containing polar solids dispersed in nonpolar grease vehicles. Application of theoretical equations to explain the influence or non-influence (adsorption or non-adsorption) of additives on grease structures containing these polar solids and non-polar liquids will be complicated by the presence of a fourth component - trace amounts of water - as well as the heterogeneous nature of the surfaces of the polar solids. Nevertheless, measurements of adsorption isotherms, heats of solution of additives in grease vehicles and heats of immersion of grease thickeners in additive solutions are being carried out. These data, although incomplete, have furnished useful information concerning the reasons for additive behavior in these more complicated systems.

The ability of some heptyl additives to fluidize greases made of Aerosil dispersed in nonpolar vehicles such as Plexol 201 or paraffin oil was believed to result from adsorption of the additive. The additive oriented polar end to the surface and formed a protective layer around the solid particle preventing flocculation by the trace amounts of water present (1). The heptyl amine and alcohol were particularly efficient thinning agents and at concentrations as low as 1 to 2 wt. %. The acid, aldehyde and chloride had little influence on this particular grease system. The behavior appeared odd since the amine and alcohol, molecules with the weakest dipoles, were most strongly adsorbed from solution; whereas, the reverse order of adsorption would be expected if the pure additives were adsorbed onto the solid from the vapor phase (3). A second surprising effect was that even large quantities of the acid or chloride did not change the consistency of an Aerosil-built grease significantly. Recent experiments have shown that all the heptyl compounds are completely miscible with the vehicles employed; hence the relative concentration, i.e., the ratio of the equilibrium concentration of the additive to its saturation value, cannot be used as a criterion for adsorption in these systems. Other experiments with more complex aromatic additives revealed a general efficiency for thinning by compounds with hydroxyl or amino groupings although the influence of these compounds decreased as the complexity of the molecule increased (2).

Greases built with solids more polar than Aerosil were investigated next. It should be recalled that the surface polarity of the solids studied increased in the order:

Aerosil < HiSil < rutile

The thinning influence of the heptyl compounds increased as the surface polarity of the solids increased. Indeed, less amine or alcohol were required to fluidize rutile-built greases than Aerosil-built

greases. In addition, all the additives except the chloride effectively thinned rutile-built greases at low concentrations. These results indicate that the heat of wetting of the rutile surface by the acid and aldehyde is large enough to influence adsorption from solution of these additives here, whereas, this heat effect is not sufficient to cause adsorption of these compounds by Aerosil.

Another factor important in solution adsorption is the affinity or lack of affinity of solvent molecules for solute molecules. A measure of this affinity can be obtained from heat of solution data for additives dissolved in grease vehicles.

Adsorption from Solution of Additives onto Thickener Solids. -

Initially, attempts were made to measure the adsorption from solution of heptyl alcohol and heptanoic acid onto Aerosil, HiSil and rutile. Solutions of additives from 3 to 12 wt. % were prepared and calibrated using a Zeiss interferometer. Exactly 2.50, 2.50, and 10.00 grams of Aerosil, HiSil and rutile, respectively, were added to 50.0 grams of solutions of known concentration. Plexol 201 and paraffin oil were the vehicles used. Both the solid and vehicle were dried before use. A dry box containing P_2O_5 was used to store the suspension of solid in the solution while equilibrium was being reached. The solid was exposed to the solutions for a period of two weeks. The solution was centrifuged and again analyzed interferometrically. No evidence was found for the adsorption of either the alcohol or the acid in these early studies. Calculations revealed that insufficient solid was used, and that changes in solution concentration due to adsorption would be too small to be noted with accuracy.

Similar measurements were made for low concentrations of the additives heptyl amine and heptyl chloride dissolved in paraffin oil. HiSil II was then added and interferometer readings were again taken after two days. The calibration curves and the curves after HiSil had been exposed to the respective solutions are shown in Figure 4. Extensive adsorption of the amine was found to take place, but no acid adsorption occurred at these concentrations. Undoubtedly the large, thinning influence of the heptyl amine on non-soap grease systems containing polar solids is due to adsorption of the additive from solution onto the thickener solid. The non-adsorbility of the acid remains to be explained. Since only two days exposure of the solid to the solution was allowed, it was not certain whether true equilibrium was reached. Much longer exposure times were studied next.

Further work was carried out to determine the influence of solid concentration, time and water content on the adsorption of heptyl alcohol from solution onto HiSil II and Aerosil III. Paraffin oil was the vehicle used in both instances. The additive and vehicle were not dried before use whereas the solid was heated at $100^{\circ}C$. in air before immersion into the solutions. Concentrations were determined before

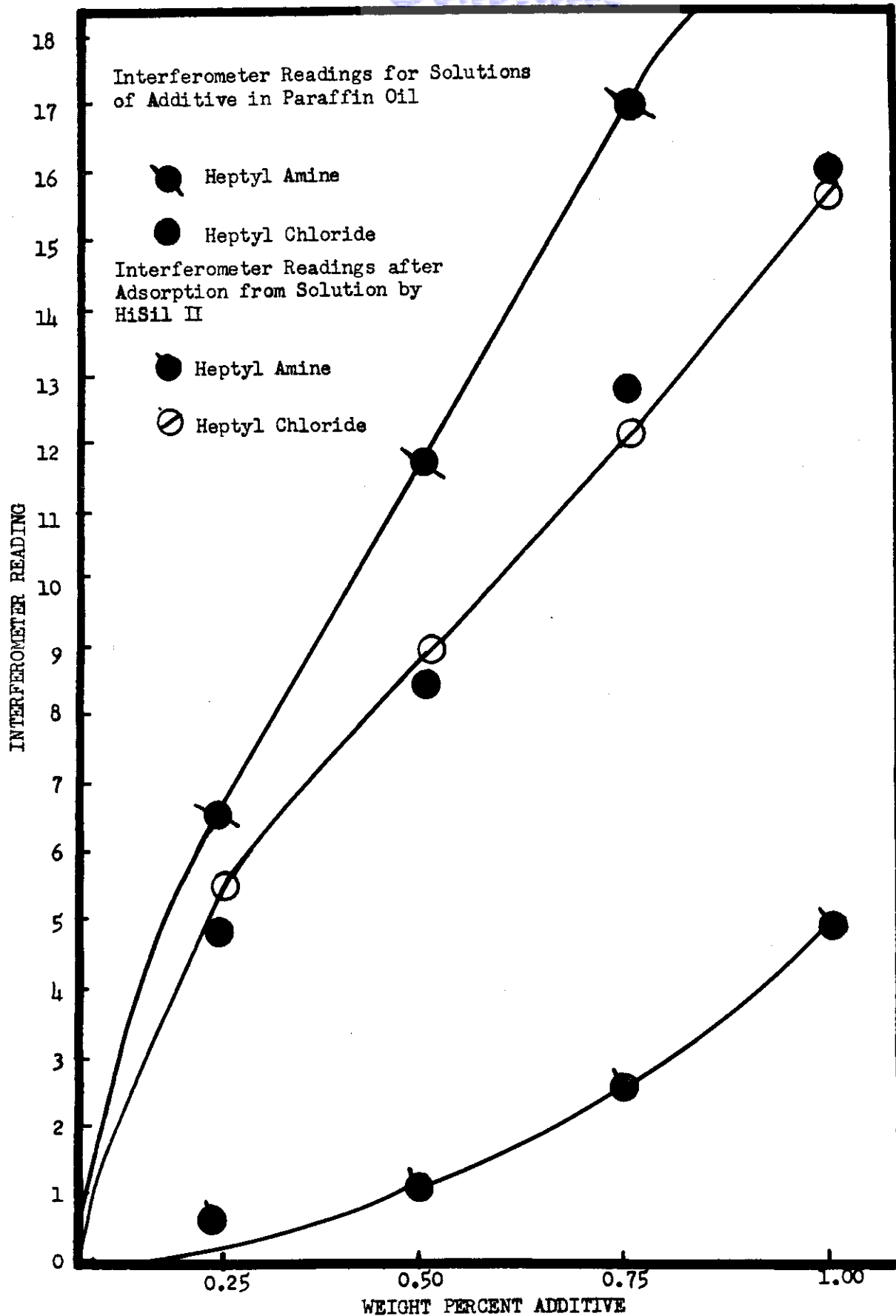


Figure 4. Interferometer Readings for Solutions of Additives in Paraffin Oil Before and After Exposure to HiSil II.

and after addition of the solid using an interferometer and in the same manner described in the preceding section.

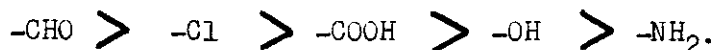
Data for the system HiSil II - heptyl alcohol - paraffin oil are plotted in Figure 5. The amount adsorbed has been calculated as millimoles of alcohol per gram of solid and plotted versus equilibrium wt. % heptyl alcohol. The first solid samples weighed 0.500 g. per 10 g. of solution. The resulting dispersions were fluid and could be agitated by shaking over the two day equilibrium period. The resulting isotherm is a typical Langmuir type isotherm generally accepted as denoting monomolecular adsorption. Indeed if the alcohol is assumed to adsorb polar end down, and if the cross-sectional area of the adsorbed alcohol molecule is taken as 20.4 \AA^2 , then the area occupied by the adsorbate is approximately $100 \text{ m}^2/\text{g}$. This figure compares favorably with the total area of this solid of $137 \text{ m}^2/\text{g}$. as determined by nitrogen adsorption.

If 1.6 g. of solid are added to the same amount of solution a grease-like paste forms after mixing with a spatula. This system should be very similar to a practical grease system. The data suggest that the same amount of alcohol adsorbs from these systems as from the more fluid, agitated solutions. Thirty day equilibrium times were used here; no attempt was made to determine when equilibrium was reached. The fact that water does not influence alcohol adsorption from solution is also evident from the data of Figure 5, at least, in the concentration range studied.

Similar results were found when Aerosil III was used as the adsorbent. This is shown in Figure 6, where data for adsorption from relatively dry solutions are plotted.

Measurement of Heats of Solution of Additives in Grease Vehicles. - Recent measurements indicated that the heptyl additives were completely miscible with paraffin oil and Plexol 201. Consequently, one driving force for the adsorption of a component from solution, the relative concentration cannot be used as a criterion to predict adsorption. In addition no adequate theory has been developed for the adsorption of miscible components from solution. For this reason the adsorption behavior of the heptyl compounds could not be predicted, a priori. The need for experimentation is obvious.

On the basis of heat of wetting measurements of polar solids is straight chain butyl compounds the adsorption potential of the various compounds was found to decrease in the order



The dipole moments of the butyl compounds decreased in the same order. Very nearly the reverse effect was found when similar compounds (the heptyl compounds) were used in dispersions of polar solids in non-polar vehicles. Obviously, the vehicle exerts a strong influence on

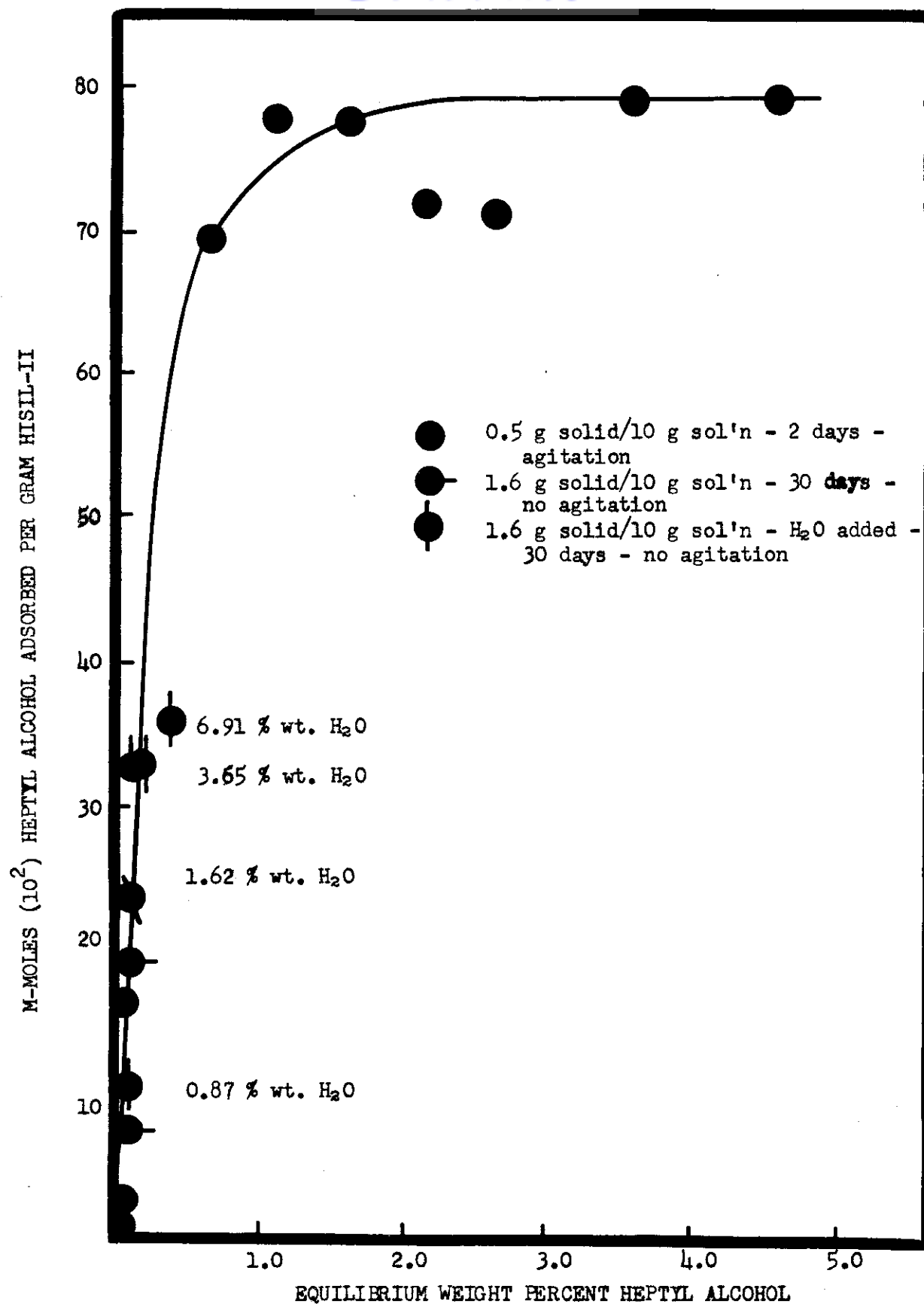


Figure 5. Adsorption of Heptyl Alcohol onto HSiL II from Paraffin Oil Solutions at 25°C.

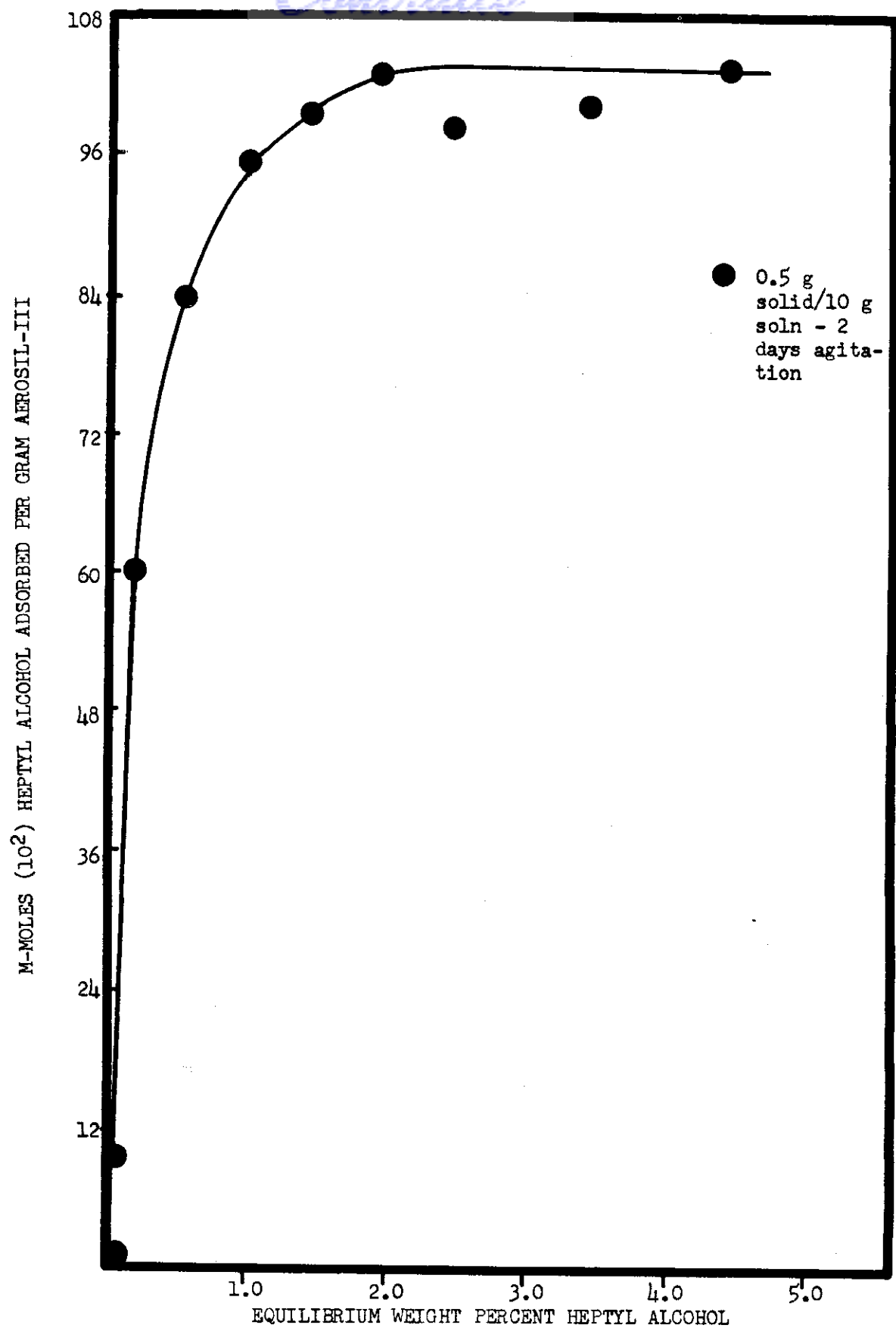


Figure 6. Adsorption of Heptyl Alcohol onto Aerosil III from Paraffin Oil Solutions at 25°C.

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the adsorptive properties of the dissolved adsorbate molecule. For example, a molecule which is attracted strongly to surrounding vehicle molecules would have a lessened ability to adsorb than a similar molecule which is attracted less or is repelled by solvent molecules. Heat of solution measurements for additives dissolved in grease vehicles furnishes a measure of the compatibility of a given additive in a given vehicle. A strong negative (exothermic) heat of solution indicates strong attraction between additive and vehicle molecules while a large endothermic heat indicates repulsion. For this reason heats of solution of the heptyl additives were measured in Plexol 201.

Heats of solution of the heptyl additives in dry Plexol 201 are plotted in Figure 7 as a function of the additive concentration. The alcohol has by far the largest endothermic heat of solution. The alcohol should adsorb most readily from Plexol 201 on the basis of this criterion and should have a large influence on the grease consistency as it does. The chloride has an exothermic heat of solution and should adsorb most poorly from solution. Indeed, the chloride was found to have little influence on greases containing Aerosil, HiSil or rutile.

The amine, an excellent thinning agent, should have a large endothermic heat of solution also. This was not found experimentally. On the contrary, extremely large exothermic heats of solution of heptyl amine in Plexol 201 were measured. It was suspected that the amine reacted chemically with an unknown amount of free acid present in the diester vehicle. Indeed, if the amine was first added to Plexol 201 and then heats of solution of additional amine were measured these heats were found to be endothermic as expected.

Heats of solution of the heptyl compounds in paraffin oil are plotted in Figure 8. Again the alcohol had the highest endothermic heat of solution and should be the most effective additive in thinning non-soap greases. The others were much lower but no exothermic heat values were found. Surprisingly the amine, also an effective additive, did not give a heat comparable to that found for the alcohol. However, other factors such as concentration or, better, activity govern adsorption from solution.

Because of the uncertainty about the purity of Plexol 201 and paraffin oil heat of solution measurements were carried out using n-heptane, B.P. 98-99°C. The heptane was dried over $MgSO_4$ and distilled before use. The heat values are listed in Table I and on the basis of this criterion alone the amine and alcohol would be expected to adsorb most strongly from solution in nonpolar liquids.

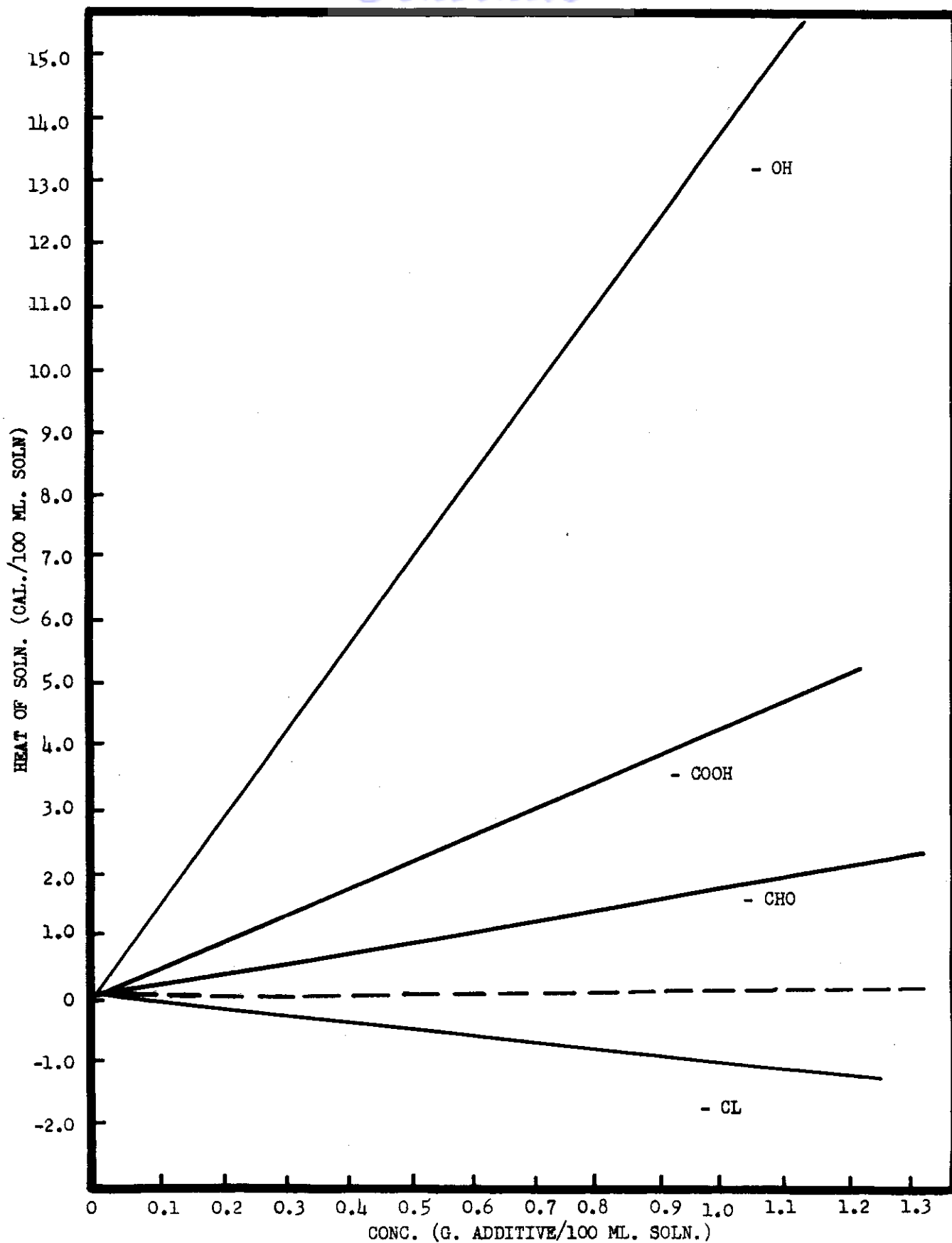


Figure 7. Heats of Solution of Heptyl Additives in Dry Flexol-201

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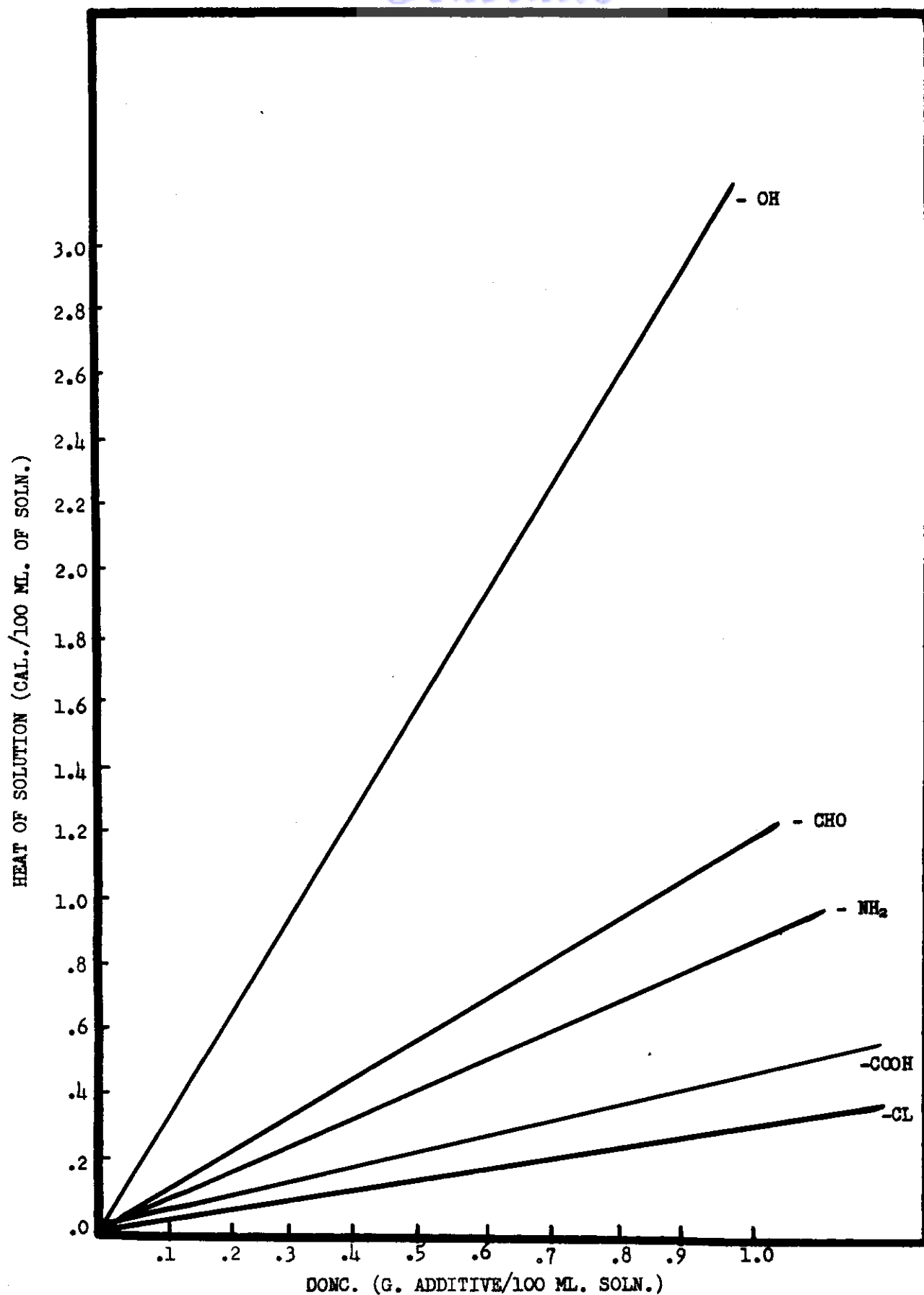


Figure 8. Heats of Solution of Heptyl Additives in Dry Paraffin Oil
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Heat of Solution of Heptyl Additives
in Heptane at 25°C

Additive	Weight Additive g	Heat of Solution cal./g. additive
Heptyl Alcohol	1.0867	42.07
Heptyl Amine	0.9775	12.08
Heptanoic Acid	1.2093	4.55
Heptyl Chloride	1.0266	3.23
Heptaldehyde	1.0384	2.46

The heat of solution of the amine in heptane is much less endothermic than the alcohol. Indeed, it had a lower heat of solution in paraffin oil than the acid. Furthermore the energy of interaction between a polar surface and the amine would be much lower than for the other additives because of the small dipole moment of the amine. For these reasons, the strong influence of the amine in thinning these grease systems could result from chemisorption of the amine onto acid sites on the surface of the polar solids employed. This uncertainty can be resolved by measuring the heat of wetting of polar solids in pure amine.

It is recognized that free energy data rather than heat data should be used to compare the adsorptive abilities of the heptyl additives from solution. However, measurements of adsorption isotherms from solution support the heat data. It has been shown that no significant adsorption of heptyl chloride onto HiSil II occurs from paraffin oil. Marked adsorption of the amine occurs in the same concentration range from 0 to 1.0 wt. % additive. Similar measurements are now in progress with Aerosil and rutile as well as other additives and vehicles.

Previous data have shown that the heat of solution of heptyl alcohol in Plexol 201 and paraffin oil is highly endothermic compared to heat of solution values for the acid, aldehyde and chloride. Taking the large endothermic heat of solution of the alcohol in these vehicles as a measure of the repulsion between solvent and solute molecules, it is not unexpected that the alcohol adsorbs from solution onto the weakly polar Aerosil surface, despite the fact that the heat of wetting of Aerosil by the pure alcohol itself, is much lower than those for the aldehyde, acid and chloride. The importance of heat of solution measurements in systems of this type is apparent when it is noted that only for the rutile-built greases is the polarity of the solid surface and consequent interaction energy between additive and solid sufficiently high to overcome the affinity of the additive for the solvent and

cause adsorption and thinning. It is significant that all the additives cause thinning of rutile-built greases except the chloride, and the chloride has the lowest endothermic heat of solution in paraffin oil and an exothermic heat of solution in Plexol 201.

Heats of Wetting of Solids in Additive Solutions. - The heat liberated when dry samples of HiSil II were immersed in additive-paraffin oil solutions was also measured. Very nearly 0.6500 g. of solid was used in each instance. The heat values are listed in Table II. The constancy of the heat values for samples immersed in solutions of heptyl alcohol in paraffin oil suggest that maximum adsorption (possibly monomolecular adsorption) of the alcohol has occurred. The heats decrease in the order

amine > alcohol > acid > chloride

which is also the order of effectiveness of these additives in greases built from this relatively polar solid. These measurements are to be extended and combined with heat of solution and adsorption isotherm measurements so that the thermodynamics of a particular additive-vehicle system can be developed as in the case of graphon-butanol-water.

TABLE II

Heat Values for the Immersion of
*HiSil II in Additive-Paraffin Oil Solutions**

Wt. HiSil g.	Additive	Wt. % Additive	ΔH total cal./g. solid
0.6614	Heptyl Alcohol	1.0	-6.37
0.6511	"	2.0	-5.43
0.6731	"	3.0	-6.09
0.6538	Heptyl Amine	3.0	-9.16
0.6502	Heptanoic Acid	3.0	-5.34
0.6648	Heptyl Chloride	3.0	-1.49

* HiSil II was evacuated at 25° for 24 hours at an ultimate vacuum of 10^{-5} min. Hg. pressure.

** The paraffin oil was dried over P_2O_5 and filtered in a dry box before use.

Continued

The influence of more complicated aliphatic and aromatic additives on greases built from polar solids has been studied using penetration measurements. Heats of solution measurements of some of these compounds are being determined to assess the value of such heat measurements as a criterion for adsorption from solution. The solution of 1.0062 g. of butanol and 1.0250 g. of nitrobenzene in 250 ml. of Plexol 201 produced endothermic heat of 26.8 and 1.47 cal/g. respectively. These values are consistent with the marked thinning ability of the alcohol compared to the nitrocompound. Other complex molecules are now being studied.

As soon as the influence of trace or larger amounts of water on heat values obtained when solids are immersed in solutions of additives, it can be determined whether heat data in Table II are sufficiently accurate to be used in conjunction with adsorption and heat of solution data to calculate important thermodynamic functions. Heat values in solutions prepared under more stringent drying conditions are now in progress.

Discussion of Adsorption and Heat Data. - While complete data for a given system has not been obtained, sufficient work has been performed thus far to discuss qualitatively the behavior of additives in grease systems containing polar solids. The important variables determining adsorption from solution are the heats of wetting of the solid by the pure additive compared to the pure vehicle, which in turn are dependent on the polarity of the solid and liquid. The heat of solution of the additive, which measures the degree of affinity between solute and solvent must also be considered. Lastly, the presence or absence of impurities such as water, cannot be overlooked when polar solids are used as adsorbents. With the weakly polar solid, Aerosil, the two heat of wetting terms are not vastly different, hence the heat of solution of the additive governs adsorption. Only those with high endothermic heats, such as the amine and alcohol, are adsorbed. With rutile, the most polar of the solids studied, the heats of wetting of pure additive are much greater than the heat of wetting by the solvent and even those additives with a strong affinity for the vehicle are adsorbed. Indeed, penetrometer measurements of rutile-built greases showed that all the heptyl additives except the chloride were adsorbed. For a quantitative interpretation of additive behavior further data are needed and is being obtained.

II. RHEOLOGICAL STUDIES OF NON-SOAP GREASE SYSTEMS

Initial studies of the flow behavior of silicas dispersed in Plexol-201 or paraffin oil were carried out at 25° using a Squibb viscometer (4). The solids and vehicles were both dried over P_2O_5 before dispersion in a Waring Blendor, but undoubtedly contained trace amounts of water picked up during dispersion. These data gave evidence of structure even at concentrations as low as 1 wt. % solid as well as increase in gel strength with increased amounts of added water. The addition of heptyl alcohol produced dispersions Newtonian (structureless) in character. These findings supported the conclusions reached earlier (1) on the basis of less sensitive penetrometer readings on non-soap grease systems concerning the mechanism of formation and stability of structure.

Recent rheological studies were carried out with dispersions of various hydrophobic and hydrophilic thickeners in grease vehicles to determine the influence of particle size, shape and surface energy on the strength of the gel formed. Flow curves for the silicas Aerosil III and HiSil II dispersed in paraffin oil are plotted in Figures 9 and 10. Again, if the presence of a yield value is taken as a qualitative indication of structure then gels persist down to low solids concentrations particularly for the solid, Aerosil. Aerosil III (198 m²/g.) is a much more effective gelling agent than HiSil II (150 m²/g.) despite the fact that HiSil has a greater surface polarity as determined by heat of immersional wetting measurements in water. Since these solids require at least trace amounts of water for flocculation at low solid concentrations, it appears that the only requirement for flocculation by this mechanism is that the solid be hydrophilic. The degree of surface polarity is of secondary importance. The greater gelling ability of Aerosil, of course, results from its larger surface area.

Figures 11, 12, and 13 contain flow curves for the hydrophobic solids, Copper Phthalocyanine and G. S. Hydrophobic Silica, as well as Permangel dispersed in paraffin oil. Permangel, normally hydrophilic, is extremely difficult to disperse in a nonpolar organic vehicle without the use of a wetting agent which, apparently, renders the Permangel surface hydrophobic. Permangel has a needlelike structure and consequently might be expected to have a narrow junction point cohesive energy spectrum which could lead to strong gel formation in dispersion. Indeed, evidence for gel structure with small concentrations of solid (less than 0.2 wt. % solid) was found rheologically when this material was dispersed in water with a Waring Blendor. No surfactant is necessary for complete dispersion in this polar liquid. On the other hand, three wt. % Permangel dispersed in paraffin oil using the surfactant Alrose "Amine S" exhibits nearly Newtonian flow behavior as illustrated in Figure 11. Although Permangel has needlelike particles and a surface area as measured by nitrogen adsorption measurements of about 250 m²/g., its gelling ability is less than

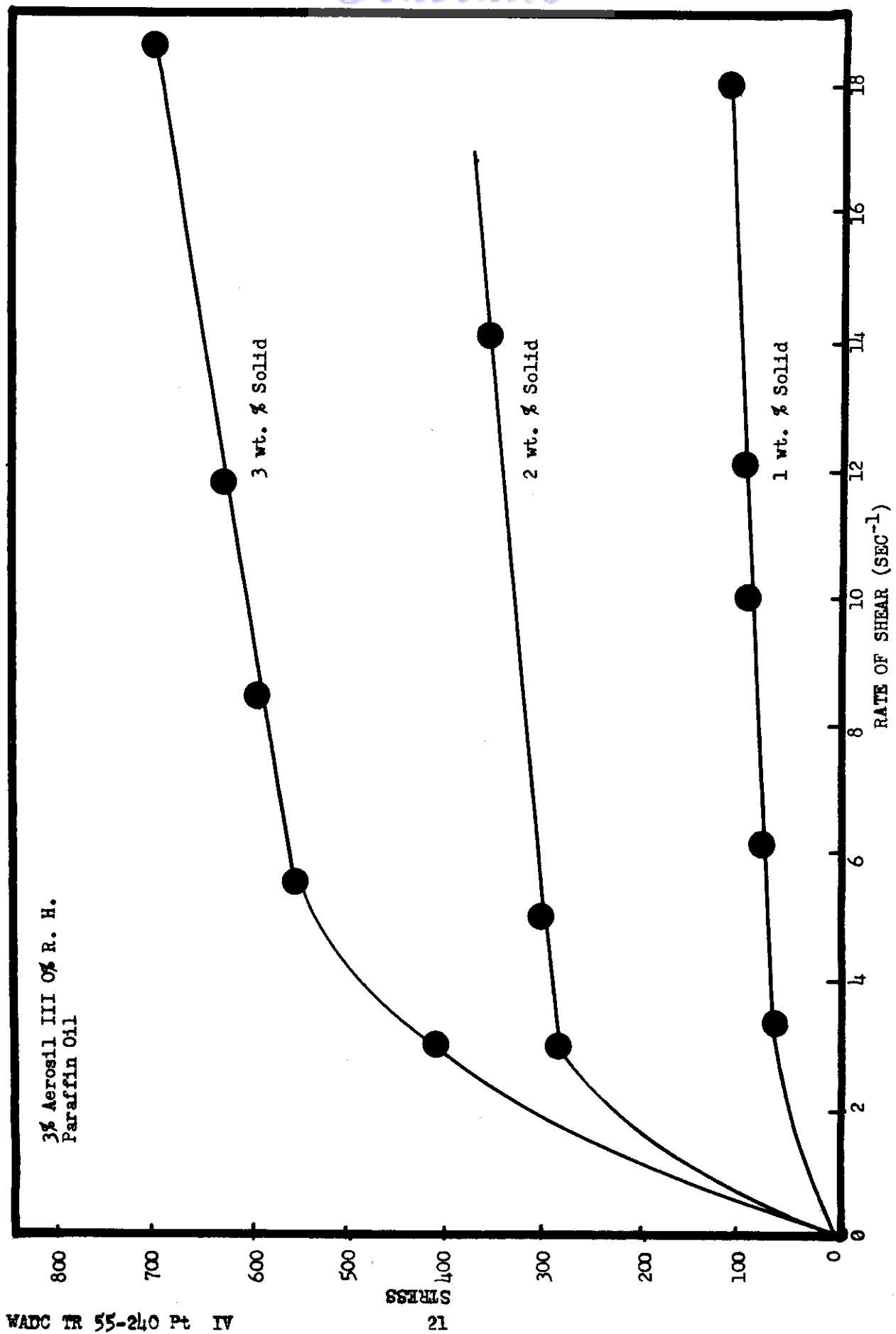


Figure 9. Flow Curves for Aerosil III (dried) Dispersed in Paraffin Oil

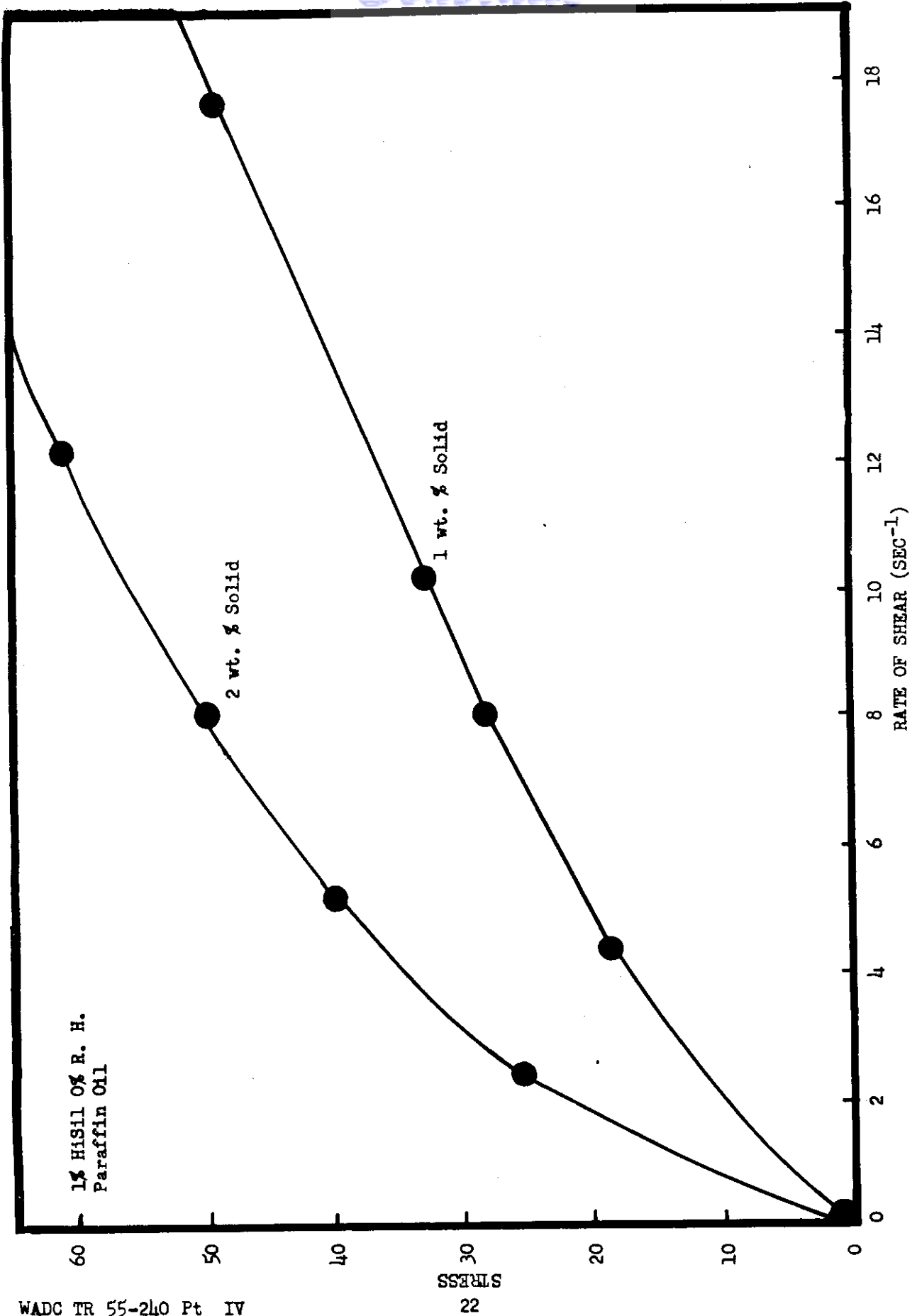


Figure 10. Flow Curves for HiSil II (dried) Dispersed in Paraffin Oil with a Waring Blendor

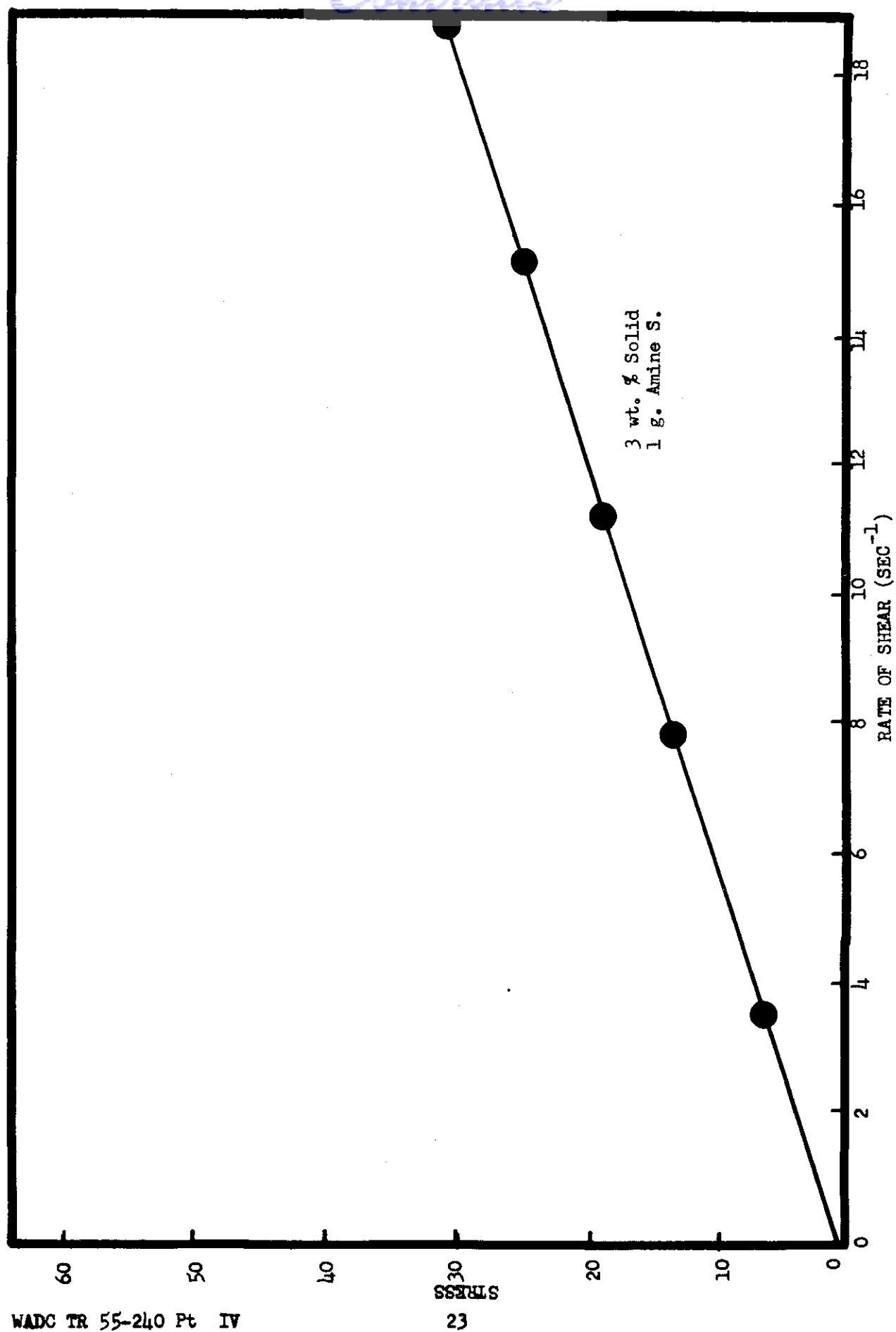


Figure 11. Flow Curves for Permangel Dispersed in Paraffin Oil

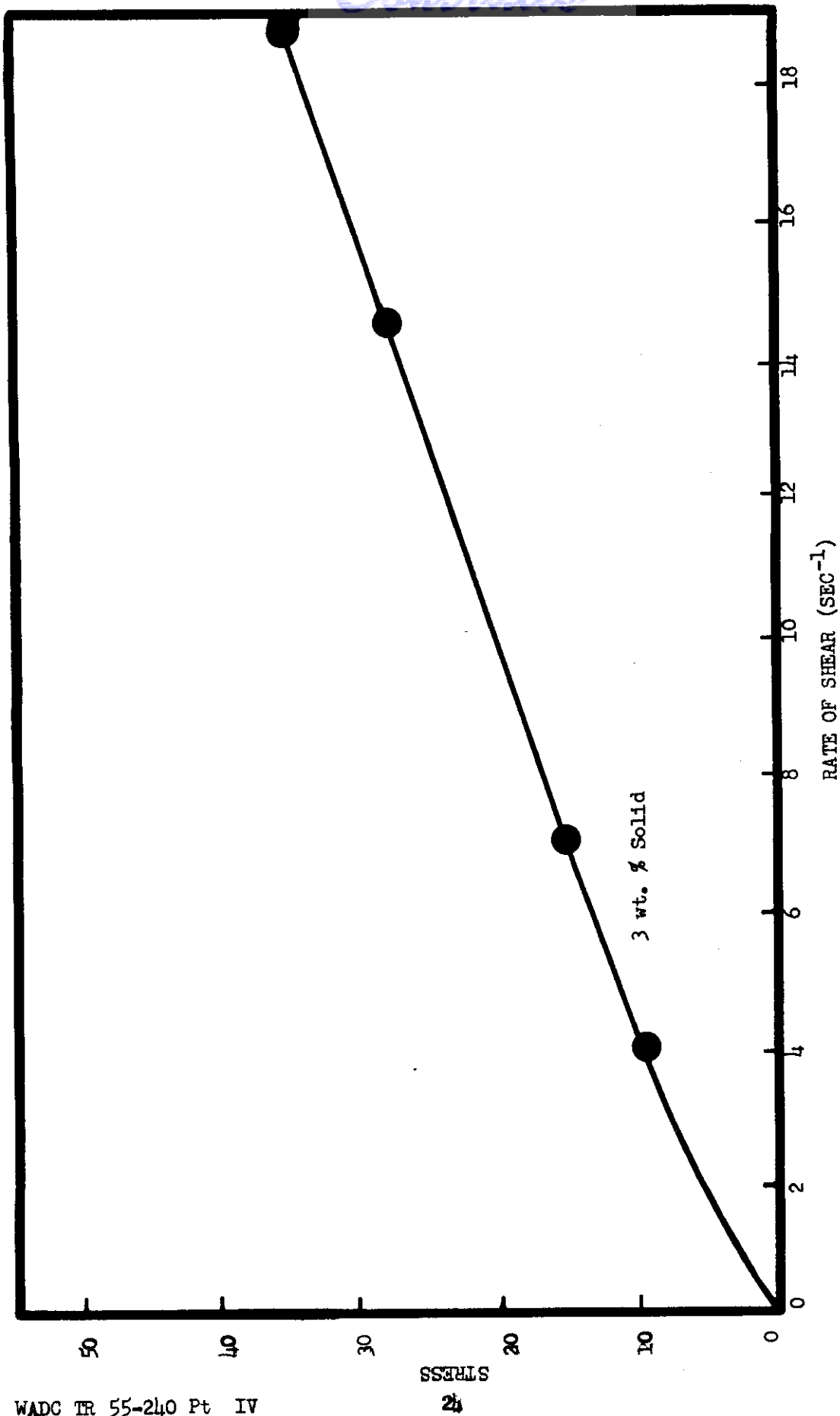


Figure 12. Flow Curves for Copper Phthalocyanine Dispersed in Paraffin Oil

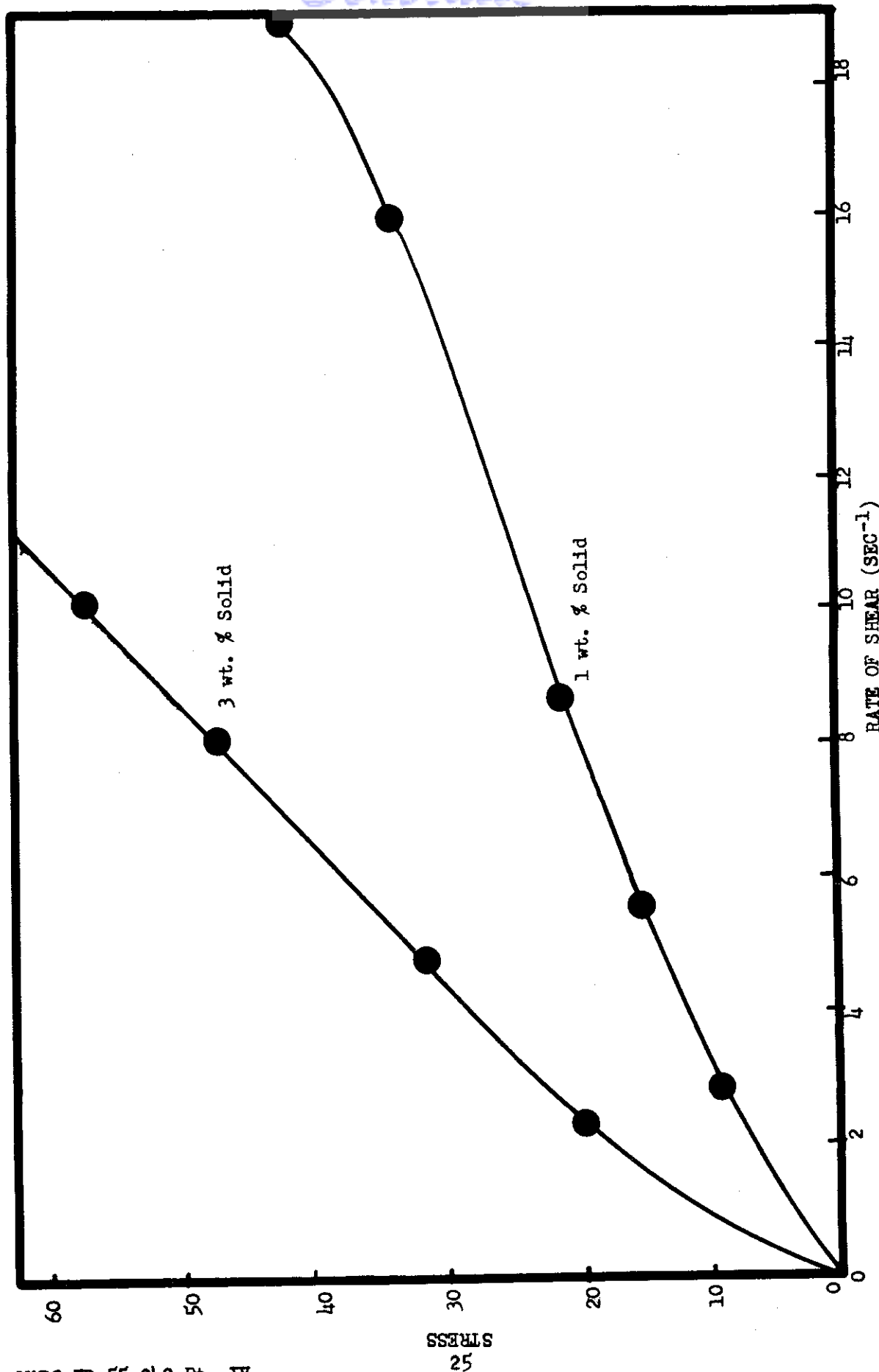


Figure 13. Flow Curves for G. S. Hydrophobic Silica Dispersed in Paraffin Oil.

either HiSil or Aerosil. This results presumably from the surface hydrophobing caused by the surfactant; hence water cannot effectively aid in the flocculation process here. These data show that the influence of small amounts of water in flocculating polar solids far overshadows the influence of either particle diameter or particle shape where the solid particles have hydrophobic surfaces.

Copper Phthalocyanine and G. S. Hydrophobic silica behave similarly to Permangel in paraffin oil. The hydrophobic silica is the more effective gelling agent possibly because of its large surface area ($\sim 300 \text{ m}^2/\text{g.}$). Again HiSil and Aerosil, although much smaller in area, are more effective thickeners because traces of water can act as a flocculating agent for these polar solids.

III. ARYLUREA GREASE THICKENERS

Because of the many good properties of arylurea thickened greases and because the possibility exists that other organic compounds will eventually find use as non-soap grease thickeners, a fundamental study of the variables influencing the formation and growth of particles or organic solids in solvents or grease vehicles has been initiated. Emphasis was placed on the arylurea prepared from National Aniline diisocyanate, Nacconate 200, p-toluidine and p-chloroaniline. However, because of the lack of raw materials, initial preparations were carried out using p-toluidine and aniline. The results of these preparative studies, irrespective of the reactants used, should be generally applicable to the preparation of any high area, organic solid.

Influence of the Method of Preparation on Grease Consistency. - Initial studies were carried out to determine whether the reactants, solvent or method of addition of reactants influenced the consistency of greases prepared at 25°C. in Plexol 201. In addition, the stability of the greases were measured after a 60 day storage in stoppered glass containers. These data on reactants used, solvent, initial and final penetration, etc., are listed in Table III. The following general conclusions can be reached from the results of these experiments; first, for the greases prepared from p-toluidine and Nacconate 200:

(a). It appears that if Nacconate 200 dissolved in either acetone or MEK is added to Plexol 201 before amine, then grease formation is not possible at this concentration of thickener (20 wt. %).

(b). A grease does form (run 4) if the Nacconate 200 is first added to Plexol 201 without the use of a solvent.

(c). Run 3 shows that a grease forms readily if the amine dissolved in acetone is first added to the Plexol, followed by the addition of the Nacconate.

TABLE III

Characteristics of Arylurea Grease Thickeners Prepared in Plexol 201 at 25°C.

No.	Wt. (g) Nacconate 200	Wt. (g) Para Toluidine	Wt. (g) Aniline	Wt. % Thickener	Method of Preparation	Initial Penetration*	Penetration After 60 Days
1.	13.2	10.7		20.0	A-A	fluid	190
2.	13.2	10.7		20.0	A-B	fluid	fluid
3.	13.2	10.7		20.0	B-A	238	166
4.	13.2	10.7		20.0	N-B	229	116
5.	13.2	10.7		20.0	M-A	fluid	251
6.	13.2		9.3	21.3	M-B	264	251
7.	13.2		9.3	15.0	N-C	292	206
8.	13.2		9.3	10.0	N-A	fluid	193

* Large penetrometer cone used in all measurements.
Grease cone ASTM D217-48. Used in all previous work.

See next page for notes on methods of preparation.

* Milled, three times before penetrometer readings, solvent removed by heating at 100° C. for 2.0 hours.

Contrails
NOTES TO TABLE III

- A-A. Nacconate 200 in acetone and p-toluidine in acetone added to Plexol together.
- A-B. Nacconate 200 in acetone first mixed with Plexol; p-toluidine in acetone next added.
- B-A. p-toluidine in acetone first mixed with Plexol; Nacconate 200 in acetone then added.
- N-B. Nacconate 200 first added to Plexol; p-toluidine then added.
- M-A. Nacconate 200 in methyl ethyl ketone (MEK) first added to Plexol; p-toluidine then added.
- M-B. Nacconate 200 in MEK first added to Plexol; aniline then added.
- N-C. Aniline added to Plexol; then Nacconate 200.
- N-A. Nacconate 200 first added to Plexol; aniline then added.

Contrails

(d). The use of MEK as a solvent leads to a grease less subject to change on standing 60 days than if acetone was used.

The following general conclusions were reached after reacting Nacconate 200 with aniline.

(e). Aniline apparently reacts with Nacconate 200 to form a grease structure more readily than p-toluidine. Run 6 shows that a grease forms with aniline even if Nacconate 200 in MEK is added to the Plexol before the amine.

(f). A grease structure forms with aniline and Nacconate 200 at a low wt. % thickener (15 wt. %), concentration. Again the important role of the reactant type is obvious.

(g). No grease forms at 10 wt. % thickener.

These data are sufficient to show that the initial consistency of an arylurea thickened grease as well as its stability after storage is a function of such variables as type of amine used, method of addition, etc. It is significant that the penetration values for all the greases tend to decrease toward a common level after storage for 60 days and remilling.

Other experiments with these reactants not reported in Table III revealed:

(h). The bleeding of grease samples is more pronounced with acetone than if MEK is used as the solvent to dissolve the reactants.

The Influence of Temperature on the Preparation of Arylurea Thickener Solids in Grease Vehicles. - The influence of temperature on the properties of an arylurea prepared from p-toluidine and Nacconate 200 was investigated. Both the amine and diisocyanate were dissolved in dry acetone. In one set of experiments the p-toluidine - acetone solution was added to dry Plexol 201 before the Nacconate - acetone solution (method BA). The reverse procedure was also used (method AB). In all instances 110 g. samples of grease were prepared and sufficient amine and Nacconate was added to yield 20 wt. % thickener in the final grease assuming complete reaction and that all the acetone was removed from the prepared grease on evacuation.

Data for the preparation of arylurea greases "in situ" from -20° to 30° C. are listed in Table IV. Here, the Nacconate 200 was added to the Plexol - amine solution held at a given temperature in a suitable bath. The Nacconate - acetone solution could not be cooled below about 10° C. because of the insolubility of the diisocyanate. Irrespective of procedure, however, 10.7 g. of p-toluidine in 10 ml.

TABLE IV

Penetration Measurements of Arylurea Greases Prepared at Various Temperatures
(Method of Preparation BA)

Mixing Temperature			Penetration as a Function of the Number of Passes on a Mill									
No.	P-toluidine in Acetone in Plexol 201	N-200 in Acetone	Final	1	2	3	4	5	6	7	8	9
9	-20°C	+11°C	- 3°C	--	--	92	92	101	101	106	107	107
10	-12°	+16°	+ 6°	--	--	92	103	103	107	114	113	113
11	- 2°	+12°	+10°	--	--	96	106	112	113	116	116	118
12	+ 2.5°	+18°	+18°	--	--	106	110	117	118	117	127	123
13	+ 6°	+12°	+19°	--	--	87	101	108	113	115	117	117
14	+10°	+12°	+21°	--	--	82	100	110	110	112	108	112
15	+15°	+15°	+25°	86	101	104	105	102	103	102	110	110
16	+20°	+17°	+30°	58	88	94	101	105	110	113	112	112
17	+25°	+17°	+35°	58	87	100	101	103	105	105	108	112
18	+30°	+20°	+39°	52	76	88	91	95	98	99	101	102

Control
of acetone, 13.2 g. of Nacconate 200 in 60 ml. of acetone were used in all preparations. After the reaction was complete the bulk of the acetone was removed at 50° C. using a water aspirator for 4.0 hours. Final evacuation was carried out for 6.0 hours at 150° C. using a mechanical pump. An ultimate vacuum of 2 mm. Hg. was reached.

It is apparent from Table IV that the penetration value of an arylurea grease is a function of the number of passes on a three roll mill as well as the temperature of preparation. At a given temperature, low penetration values were found after one or two passes. The penetration values increased with the number of passes but became essentially constant after 8 or 9 passes. The increase in penetration* with number of passes is difficult to explain.

It does not appear that samples milled only two or three times are true dispersions, for despite their lower penetration values, these samples tend to bleed seriously. This behavior is not nearly so severe after maximum milling has been carried out. Data of Table IV also show that when the amine is added to the grease vehicle prior to the diisocyanate, there are not marked differences in the final consistencies of greases prepared at temperatures from -20° to 30° C. Only small differences, however, were found.

Data for greases prepared at various temperatures are also given in Table V. Here, the Nacconate 200 was added to the grease vehicle prior to the addition of the amine. As found in the initial studies of arylurea grease formation, this method of addition produced greases with less structure (higher penetration values) than if the amine was added first. Further, a marked increase in penetration was found with increase in temperature of preparation from -10° to 20° C. This is not unexpected since at low temperatures (and perhaps low solubility of the arylurea) many nuclei would be expected to form on rapid addition of reactants. Hence, higher area particles might well be expected to form at the lower temperatures yielding greases of lower penetration.

The marked differences in greases prepared by the two methods of mixing are illustrated in Figures 14 and 15. Greases prepared by method BA are much less sensitive to consistency changes with temperature than are greases prepared by method AB.

* A new Micro Penetrometer cone was used in all these measurements. This 5/8" plastic cone and plunger weighed 19.0 g. and was supplied by Precision Scientific Co. Penetrometer values with this cone are being correlated with values obtained with the large cone originally used.

TABLE V
Penetration Measurements of Arylurea Greases Prepared at Various Temperatures
(Method of Preparation AB)

Mixing Temperature			Penetration as a Function of the Number of Passes on a Mill									
No.	N-200 in Acetone - Plexol 201	P-toluidine in Acetone	Final	1	2	3	4	5	6	7	8	9
19	-10°C	+10°	+ 2°C	59	63	89	108	109	111	112	115	115
20	- 1°	+10°	+11°	77	101	111	111	116	118	118	122	123
21	+20°	+10°	+30°	68	104	113	122	129	133	137	134	144

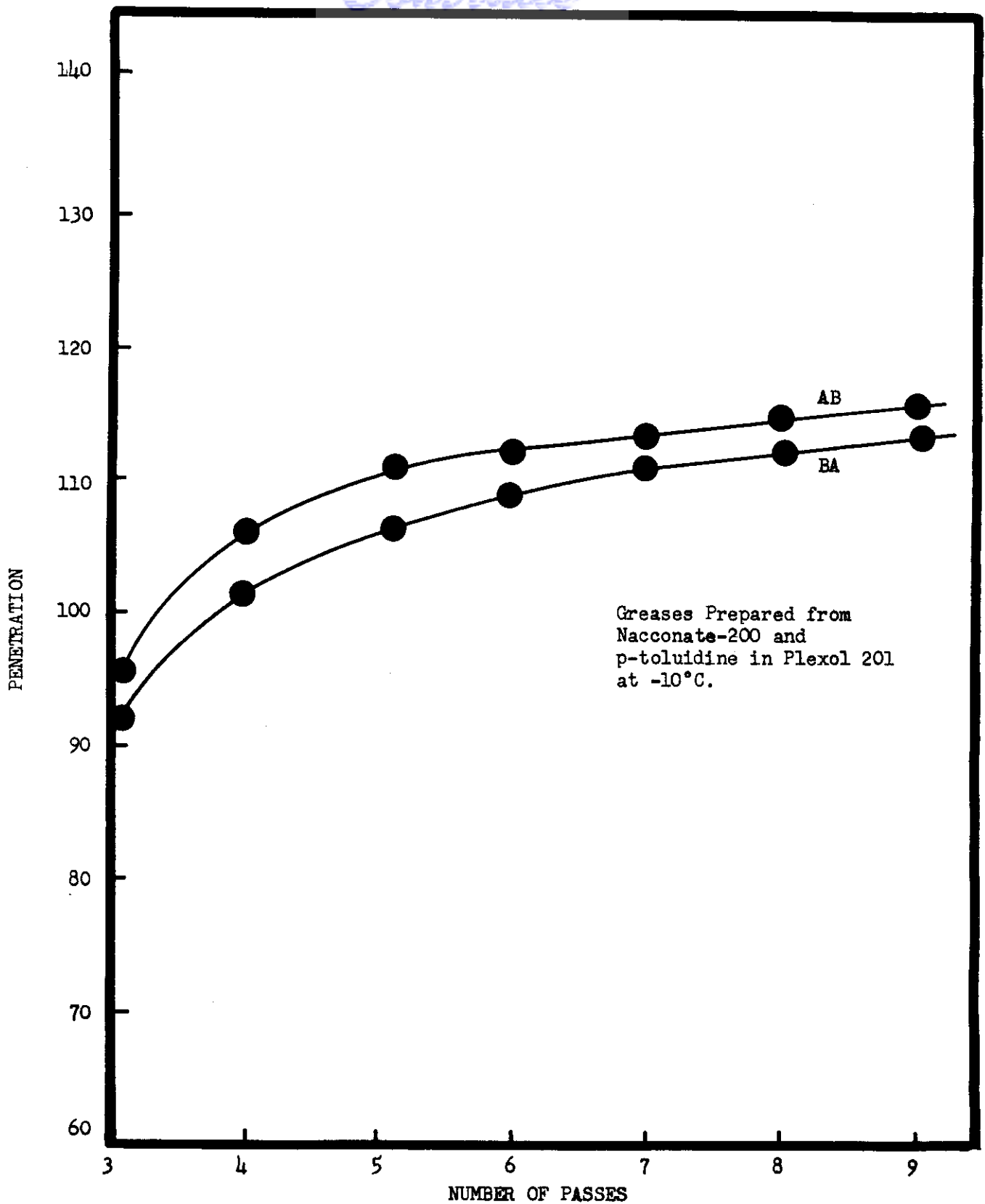


Figure 14. Penetration vs. Number of Passes on a Three Roll Mill for Arylurea Greases Prepared at -10°C.

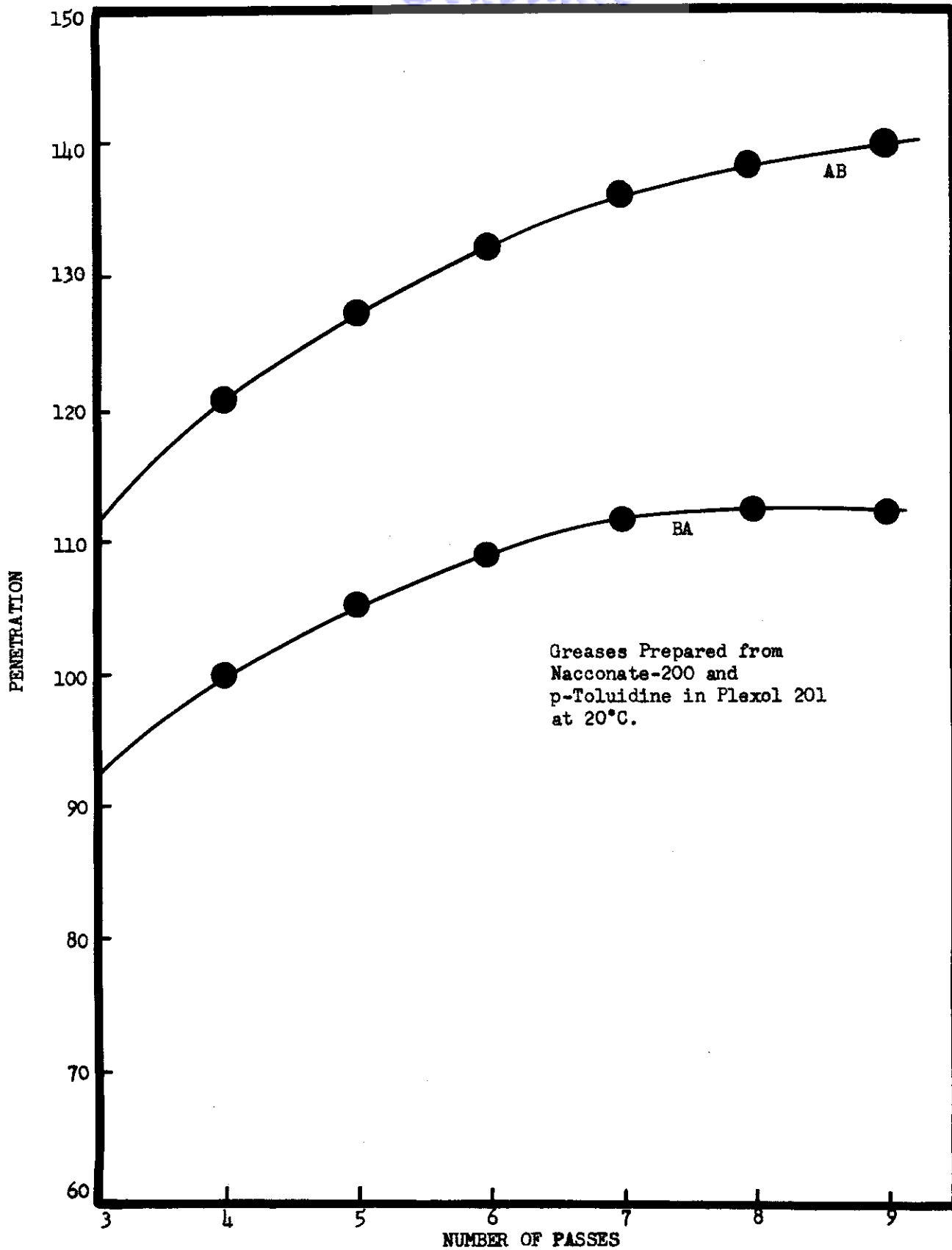


Figure 15. Penetration vs. Number of Passes on a Three Roll Mill
for Arylurea Greases Prepared at 20°C.

Arylurea Grease Thickeners Prepared from Nacconate 200, p-Toluidine and p-Chloroaniline. - The fundamental study of the many variables which influence the formation and growth of organic solid particles in solvents or grease vehicles was continued. Because of the lack of raw-materials, initial studies were carried out using aniline and p-toluidine. Emphasis was placed on the arylurea prepared from Nacconate 200, p-toluidine and p-chloroaniline in the studies reported below.

Arylurea Grease Preparation as a Function of Temperature. - The properties of arylurea greases prepared in the same manner but at different temperatures are shown in Table VI. Greases were formed in the following manner: 13.20 g. of Nacconate 200 in 60 ml. of acetone was added to 99.60 g. Plexol 201. To this was added 5.35 g. of p-toluidine and 6.35 g. of p-chloroaniline in 25 ml. of acetone. At least four hours was then allowed for completion of the reactions. The grease was then pumped at 65° C. for 24 hours using a water aspirator, followed by heating at 80° in an oven overnight and finally by pumping at 65° using a mechanical pump. It is believed this treatment removed most of the solvent. The sample was milled, penetration measurements taken and then stored.

The data shown in Table VI again shows that temperature has a pronounced influence on the final consistency of a freshly prepared arylurea grease if the amines were added to a solution of Nacconate 200 in Plexol 201. Greases prepared at temperatures from 10° to 30°C. were much too fluid after about 6 passes on the three roll mill for penetration measurements. The samples were then stored for 30 days. All the samples bled badly. After remilling, however, all the greases had very nearly the same consistency as revealed by the micropenetro-meter readings. These data suggest that much finer arylurea particles develop during preparation at low temperatures with consequent increase in gel structure and lower penetration. The similarity of grease consistency after storage for 30 days and remilling is as yet unexplained unless agglomeration occurs on standing.

Greases were next prepared without the use of a solvent from p-toluidine, p-chloroaniline and Nacconate 200 in Plexol 201 at 25° C. Here the ratio of p-chloroaniline to p-toluidine was varied although two moles of amine were always reacted with one mole of the diisocyanate. It is quite apparent that greases prepared from the pure amines or with a large excess of a given amine have greater structure as revealed by the penetration measurements. Storage for one day and remilling again revealed an increase in consistency. These data are listed in Table VII.

Apparently when Nacconate 200 is added to a mixture of p-chloroaniline and p-toluidine in a grease vehicle there is a marked difference in the rates of reaction of the amines with the diisocyanate.

Contrails

TABLE VI

Penetration Measurements of Arylurea Greases Prepared from p-Toluidine, p-Chloroaniline and Nacconate 200 in Plexol 201 at Various Temperatures. (20 wt. % solid)

Run No.	Temp. °C	Penetration as a Function of the No. of Passes									Penetration after Storage 30 Days 9 Additional Passes
		1	2	3	4	5	6	7	8	9	
22	-20	92	105	111	114	117	160	120	122	125	93
23	-10	82	98	103	109	110	114	116	122	120	86
24	0	87	102	109	113	127	128	131	136	142	97
25	10	110	131	148	154	178	190	*	*	*	92
26	20	99	120	132	151	160	*	*	*	*	98
27	30	125	148	167	197	205	*	*	*	*	132

* Too fluid

TABLE VII

Penetration as a Function of the Ratio of p-Chloroaniline to p-Toluidine Added to a Solution of Nacconate 200 in Flexol 201 (20 wt. % solid).

Run No.	Ratio p-chloroaniline p-toluidine	Penetration as a Function of the Number of Passes									Penetration after Storage 1 Day, 9 Additional passes
		1	2	3	4	5	6	7	8	9	
28	100/1	50	59	64	66	66	70	72	75	76	64
29	80/20	85	101	108	114	119	118	125	126	127	75
30	60/40	111	125	135	147	145	155	165	178	178	100
31	50/50	115	113	122	123	124	127	131	140	145	92
32	40/60	86	94	102	102	102	102	106	110	115	90
33	20/80	64	82	85	87	88	91	97	102	103	75
34	1/100	57	75	83	90	90	89	87	91	87	44

a. No solvents used.

b. The amines were dispersed in Flexol 201 first. The Nacconate 200 was then added. Grease prepared at room temperature.

Contrails

To study this effect further, greases were prepared not only at different ratios of the amines as before, but also under different conditions of mixing. The mixing conditions and results obtained are listed in Table VIII. In method A, the p-chloroaniline was added to the diisocyanate in Plexol 201 before the p-toluidine. In method B, the p-toluidine was added before the chloroaniline. It was observed qualitatively that the rate of reaction and evolution of heat was much less when p-chloroaniline reacted with the Nacconate 200; behavior which obviously leads to smaller particles and greater structure in the finished grease. Smaller particles would also be expected as the amount of p-chloroaniline increased and this was indeed the case for method A. The fact that different products are formed at different ratios of the amines and under different mixing conditions must also be considered in interpreting the results of these experiments. Indeed, much more effort is required before a quantitative picture of particle growth in solution can be offered.

The effects of solvents on the properties of arylurea greases was also studied. The results are listed in Table IX. Bleeding was found to be much more pronounced if a grease was prepared using solvents to dissolve the reactants. Furthermore, the use of solvents lead to greases with less structure as evidenced by the high penetration readings for these systems compared to greases prepared without solvents. Of the solvents used benzene gave better results than acetone, while MEK could not be used. The ease or difficulty of removing the solvent undoubtedly played a prominent part in determining the penetration value of the grease.

Miscellaneous Studies in the Preparation of Arylurea Greases. - The properties of arylurea greases prepared in the same manner in Plexol 201 but at different temperatures are listed in Table X. The temperatures employed were generally higher than those studied previously. A definite trend toward lower consistencies for greases made at the lower temperatures was found. Penetration measurements on these greases were not made after storage for one to two month periods.

TABLE VIII

Penetration Readings of Arylurea Greases Prepared at 25°C Using
a Variety of Mixing Conditions

Run No.	Weight Percent		Method of Mixing	Penetration After 6 Passes
	p-chloroaniline	p-toluidine		
35	80	20	A	63
36	60	40	A	72
37	50	50	A	74
38	40	60	A	83
39	20	80	A	86
40	80	20	B	90
41	60	40	B	139
42	50	50	B	126
43	40	60	B	127
44	20	80	B	91

A. Mix p-chloroaniline into Plexol 201 first, add Nacconate 200 and finally p-toluidine.
Let stand at least four hours before milling.

B. Mix p-toluidine in Plexol 201 first, add Nacconate 200 and finally p-chloroaniline.
Let stand at least four hours before milling.

C. 20 wt. % solid. No solvents used.

TABLE IX

The Influence of Various Solvents in the Preparation of Arylurea Greases* (20 wt. % solid).

Run No.	Solvent	Temp. °C	Penetration as a Function of the No. of Passes								
			1	2	3	4	5	6	7	8	9
45	acetone	10°	87	102	109	113	127	128	131	136	142
46	benzene	10°	73	85	94	100	100	102	102	102	105
47	none	22°	57	68	74	75	77	79	83	85	86
48	MEK	10°					Too Fluid				

* Grease made by adding p-chloroaniline to a solution of Nacconate 200 in Flexol 201.

TABLE X

Influence of Temperature on Arylurea
Greases Prepared by Method A.
(20 wt. % Solid)

Run Number	Mixing Temperature	Method of Mixing	Penetration after 6 passes	Remarks
49	50°C	A	79	Equal polar quantities of p-toluidine and p-chloroaniline.
50	80°C	A	87	
51	100°C	A	95	

A. Mix p-chloroaniline into Plexol 201 first, add Nacconate 200 and finally p-chloroaniline rapidly. Let stand at least four hours before milling. No solvents used.

In the last report, measurements of this type on one group of arylurea greases showed that storage often produced greases with very nearly the same penetration after remilling despite the fact that the greases were prepared at different temperatures and also had different initial penetrations.

Previously, the influence of the method of mixing and of varying ratios of p-chloroaniline and p-toluidine on the consistency of the prepared grease was investigated at 25°C. In method A the p-chloroaniline was first added to Plexol 201, followed by the Nacconate 200 and finally by the p-toluidine. The grease was allowed to stand four hours and the penetration was measured after six passes on the three roll mill. In method B the procedure was the same except that the order of addition of the amines was reversed. Method B produced greases of significantly higher penetration than found with method A. It was observed qualitatively that the rate of reaction and evolution of heat was much less when p-chloroaniline was added first; behavior which obviously leads to smaller particles and greater structure in the finished grease. Similar studies were carried out at a much lower temperature (-10°C) and the results are shown in Table XI. A decrease in penetration of the finished greases was found irrespective of whether method A or B was employed. However, the change was slight for greases prepared by method A, but amounted to as much as 50% for greases prepared by method B.

Contrails

TABLE XI

Penetration Values for Arylurea Greases Prepared at -10°C
Using Different Mixing Conditions

Run	p-chloro-aniline	Wt. Percent p-toluidine	Method of Mixing	Penetration after Six Passes
52	80	20	A	69
53	60	40	A	76
54	50	50	A	73
55	40	60	A	74
56	20	80	A	75
57	80	20	B	86
58	60	40	B	86
59	50	50	B	80
60	40	60	B	80
61	20	80	B	75

Some recent arylurea grease preparations were carried out in different grease vehicles. The procedure was to add 1.590 g. of p-chloroaniline to 24.92 g. of vehicle, followed by 3.30 g. of Nacconate 200. Then 1.34 g. of p-toluidine was added either at once or in four equal portions over a two hour period. The results are listed in Table XII for experiments carried out at 25° and 0°C. For greases prepared at 25° there appears to be a significant difference in consistency due to change in vehicle. However, fast or slow addition of the p-toluidine did not significantly alter the final consistency of the prepared grease. As noted before, decrease in temperature of preparation leads to greases with very nearly the same consistencies despite the use of different vehicles.

Preparation of Arylurea Greases in Different Vehicles

Run No.	Vehicle	Penetration After Six Passes	Remarks
		25°	
62	Circo Light	77	p-toluidine added fast
63	Paraffin Oil	85	"
64	MLO 8200	91	"
65	Plexol 201	101	"
66	MLO 8200	87	p-toluidine added slowly
		0°C.	
67	Paraffin Oil	66	p-toluidine added fast
68	Circo Light	76	"
69	MLO 8200	82	"
70	MLO 8200	74	p-toluidine added slowly

Arylurea Grease Thickeners Prepared in Solvents. - Thickener particle size is much more difficult to vary in viscous, grease vehicles than in the ordinary solvents such as benzene, acetone, MEK, etc. For this reason it was decided to determine the influence of such parameters as concentration, temperature and addition on the surface characteristics of grease thickeners prepared in and isolated from such solvents. Thus far fifteen different grease thickeners have been prepared from p-toluidine, p-chloroaniline and Nacconate 200 using either acetone, benzene or MEK as solvents. Beside solvent type, the influence of temperature and rate of addition was investigated. Most of the thickener solids have been isolated from the solvents by filtration and evacuation. Surface area and heat of immersional wetting measurements of these solids are now in progress, and some conclusions concerning the influence of variables on the surface characteristics of these solids can be made.

Arylurea thickeners were prepared in the following manner: 6.60 g. of Nacconate 200 was dissolved in 150 ml. of solvent. To this was added 2.68 g. of p-toluidine and 3.18 g. of p-chloroaniline dissolved in 50 ml. of a different sample of the same solvent. The two solutions were cooled first to the chosen temperature before mixing. Several variables were studied. The amines were either added to the Nacconate solution rapidly or in three equal portions over a period of 0.5 hour. After amine addition, the mixture was stirred over a period of 1.0 hour. The solvent was either removed by evaporation at room temperature using a water aspirator or by filtration and

final drying by evacuation. The arylurea powders were stored over at 25° over P₂O₅ before area measurements were made using nitrogen adsorption at -195°C.

Surface area measurements are reported in Table XIII for arylurea greases prepared in solvents. All materials were undried before use and contained variable quantities of water. Tentative data now available shows that the water content of the components before preparation of the grease profoundly affects the final product, hence certain inconsistencies in data can be adequately attributed to unknown and variable water content. The variability should be much greater when acetone is used. To reiterate, the presence of water leads to a rather drastic increase in particle diameter and consequent higher penetration of greases prepared with such solids. These data cannot be quantitatively discussed, unfortunately. Generally, temperature influences particle size; in most instances, the lower the temperature the higher the surface area of the finished solid. This is reasonable for reasons discussed in the preceding section. Smaller area particles are found when addition of amine to Nacconate solutions is prolonged. This is not true for the materials prepared in benzene, but the variation in properties of thickener particles with change in condition has been found to be small when prepared by other techniques in this solvent. The effect of solvent on particle size is evident. It is well to remark that the surface areas are small when prepared by these techniques (removing all solvent by evacuation), as will be demonstrated in the second next section, due to the presence of water, undoubtedly.

TABLE XIII

Surface Areas of Arylurea Thickener Solids
(Prepared in Solvents)

Solvent*	Method of Addition of Amines	Temp. °C	ΣN_2 m ² /g.
Acetone	Fast	0°	15.7
		25°	13.5
	Slow	15°	12.4
		25°	14.2
Benzene	Fast	0°	18.4
		25°	17.3
	Slow	25°	18.1

* Solvent removed by evacuation.

Materials were not dried before use.

A sharp increase in area was found for materials prepared in benzene if the bulk of the solvent is removed first by filtration compared to solvent removed by evacuation exclusively. These data are tabulated in Tables XIV and XV respectively. The influence of solvent is greater in this series although different solvents were used except for benzene in these later studies. Again smaller areas are found with slow addition of the amine. While trends shown are valuable it is important to re-emphasize that the unknown water content makes accurate conclusions impossible.

TABLE XIV

Surface Area of Arylurea Thickener Solids
(Prepared in Benzene)

Solvent*	Method of Addition of Amines	Temp. °C	ΣN_2 m ² /g.
Benzene	Fast	10°	32.5
		25°	31.3
	Slow	15°	31.9
MEK	Fast	0°	13.5
		10°	14.4
	Slow	15°	
		25°	10.2
Ethyl Acetate	Fast	25°	20.0

* Solvent removed by filtration and evacuation.

Materials were not dried before use.

The results of preliminary experiments in dry benzene are tabulated in Table XV. These data although unchecked will be more reliable when more determinations are carried out. The increase in area on drying compared to other techniques is great particularly at low temperature preparations. Again a decrease in particle diameter was found with decreasing temperature. More extensive measurements are in progress using dry materials.

Surface Area of Arylurea Thickener Solids
(Prepared in Dry Benzene)

Solvent*	Method of Addition of Amines	Temp. °C	$\frac{1}{2}$ N ₂ m ² /g.
Benzene	Fast	0°	46.0 - 47.3
		10°	33.2 - 34.1
		25°	34.3 - 34.4

* Solvent removed by filtration.

1. Chessick, John J. and Zettlemoyer, A. C., WADC Technical Report 55-240 Pt. III, Basic Factors in the Formation and Stability of Non-Soap Lubricating Greases, December 1956, Surface Chemistry Laboratory, Lehigh University, Bethlehem, Penna.
2. Young, G. J., Chessick, J. J. and Healey, F. H., J. Phys. Chem., 60, 394 (1956).
3. Chessick, J. J., Zettlemoyer, A. C., Healey, F. H. and Young, G. J., Canadian Journal of Chemistry, 33, 251 (1955).
4. Myers, R. R. and Zettlemoyer, A. C., J. Soc. Plastics Engrs., 11, 43 (1955).

LITERATURE SURVEY

General and Theoretical: Non-Soap
Greases, Gel Systems and Gel Structure

1. Bowden, F. P., Proc. Third World Petrol. Congress
(The Hague), VII, 328 (1951). The Mechanism of Boundary Lubrication.

Electron diffraction studies of the structure and orientation of lubricant films are described and the influence of temperature on the orientation and frictional behavior of the film is discussed. The importance of chemical attack is emphasized. Breakdown of film investigated by radioactive tracer and other sensitive methods.

2. Kadmer, E. H., *ibid*, 343 (1951). The Problem of Lubricity in the Machining and Working of Metals.

The effect of pressure on the viscosity of lubricating oils increases with increase in sp. gr. of oil. Effect of pressure up to 3000 atm. on viscosity of petro. oils, fatty oils and chlorinated hydrocarbons is given. Fatty oils show less increase in viscosity at high pressures than petroleum oils. This is important for severe drawing operations where high pressures occur. Surface reactions of oil constituents are discussed and a distinction is made between protection by a lubricant film and a chemisorbed species.

3. Smalheer, G. V. and Mastin, T. W., Petroleum Processing,
7, 1780 (1952) Phosphorus in the Lubricants Field.

A review of P compounds used in oils and greases.

4. Vinogradov, G. V. Ledatel Akad. Nauk Azerbaidzhan S. S. R.
Baku, 151 (1953) Lubricating Greases as Disperse Systems.

Describes optical and election - microscopic studies of grease systems.

5. Keil, G. and Presting, W., Chem. Tech., (Berlin) 6, 436
(1954). Structure Study of Greases II. Rheological Determination of Structure and Heat Stability.

The structure stability of greases was determined from measurements of apparent viscosity of a grease at different shear stresses and at various temperatures. A good grease was defined as one which shows the greatest recuperation in apparent viscosity after 24 hours rest. The heat stability was determined by measuring viscosity at 20°C and 60°C.

6. Akira, W., J. Oil Chemists Soc. (Japan) 3, 247 (1954), Review.

A survey of recent advances in grease technology.

7. Dreher, J. L., Carter, C. F., and Reid, E. B., NLGI Spokesman, 18, 8 (1955). Some New Approaches to the Measurement and Prediction of Apparent Viscosity of Lubricating Greases.

8. Hotten, D. W., ibid, 19, 14 (1955). Optical Studies of Lubricating Grease Structure.

Optical studies indicate that the most important properties of gelling agents are particle size and shape, stickiness and strength. In general, the finer the particle size the greater the thickening ability. An unsymmetrical particle is preferable. Stickiness (adhesion) accounts for rigidity of grease while strength of individual particles is important in resistance of grease to shearing forces.

9. Leet, R. H., ibid, 19, 20 (1955). Thickener Particle Dimensions and Lubricating Grease Consistency.

Changes in consistency and particle size of thickener of 13 greases were measured after working and aging. As the grease softened with working the length to width ratio of thickener particles decreased; as the grease aged the ratio increased. For four greases the ratio decreased after working but rapid hardening, independent of the ratio, occurred on aging. The results suggest two factors are important in structure formation, namely, particle shape and interparticle attraction.

10. Puddington, I. E., ibid, 19, 10 (1955). The Structure of Lubricating Greases.

The thickening agent must be thermally stable to give a satisfactory grease structure. The attraction between particles must not be temperature sensitive. The particles should be small so that the volume corresponding to the required amount of thickener is low. The particles should also be dimensionally stable to working.

11. Vold, Marjorie J., ibid, 19, 24 (1955). Forces Responsible for Lubricating Grease Structure.

A discussion of the role of nonpolar and polar van der Waal's forces and the formation of structure in greases.

12. McClellan, A. L. and Cortes, J. Jn., Petroleum. Engr., 28, 49 (1956). Structure of Lubricating Grease Thickeners.

Thickeners were isolated from greases and studied with an electron microscope. Structures are described.

13. Volovick, G. and Lazarre, F., Compt. rend., 242, 1986 (1956). The Lubricity of Lubricants in the Presence of CO_2 as a Function of the Dielectric Constant at Various Pressures.

The dielectric constant of mixts. of carbon dioxide and three oils was measured at pressures from 0 to 60 kg./cm². Lubricity increased with an increase in dielectric constant.

Additives

14. Elliot, Jerome S., U. S. Pat. 2, 691,000 (1954).

The load-carrying capacity of mineral lubricating oils is enhanced by the addition of 0.5 to 10% of an ester having the general formula $\text{ROOCCCH}_2 \text{X}_n \text{CH}_2 \text{COOR}$ where R is an alkyl, cycloalkyl or aryl radical which may contain halogen substituents; X is Se, Te or S and n is 2 to 4.

15. Hamilton, L. A. and Feasley, C. F., U. S. Pat. 2,689,251 (1954).

The reaction of a polyhalomethane with an unsaturated acid or its ester in the presence of a catalyst forms a material for use as an extreme-pressure additive.

16. Hook, E. O. and Thomas, W. D. Jn., U. S. Pat. 2,695,273 (1954).

The lacquer-forming tendency of crankcase oil containing alkylidene bisphenols as oxidation inhibitors is decreased by the addition of 0.3 to 5% basic petroleum sulfonates.

17. Kolfenbach, J. J. and Vesterdal, H. G., U. S. Pat. 2,696,470 (1954).

To prevent separation of carbon black from lubricating oils, the solid is coated with alkali metals, alkaline earth, aluminum or lithium soaps. Lubricant is thickened first with 1-5% soap and then 5 to 15% carbon black.

18. McCarthy, Paul and Orem, Thomas, U. S. Pat. 2,704,276 (1955).

Resistance to water is increased if certain polymers are incorporated in greases containing bentonite treated with organic bases. The polymer can consist of polymerized ethylene or esters of acrylic acid.

19. Blattenberger, John W., U. S. Pat. 2,752,310 (1956).

High temperature gelation of greases containing colloidal SiO_2 can be prevented by diols having 6-12 c-atoms/molecule.

20. Marshall, W. A. and Steininger, C. F., U. S. Pat. 2,766,205.

Five to 35 wt. % quinoline or lower alkyl-substituted quinoline can render water resistant greases thickened with inorganic solids such as an SiO_2 aerogel.

21. Marshall, W. A. and Steininger, C. F., U. S. Pat. 2,751,349.

SiO_2 aerogels are made water resistant by treatment with tin halides.

22. Peterson, W. H. and Skei, T., U. S. Pat. 2,748,081.

Lubricating greases formed from SiO_2 and a mineral oil and containing hydrophobic surfactants (I) are rendered more water resistant by the addition of 0.1 to 1 wt. % alkali metal salt or hydroxide. The (I) is preferably an aliphatic hydroxyamine.

23. Weihe, A. and Schweitzer, Otto, U. S. Pat. 2,739,121.

The thickening agent in certain non-soap greases is made water resistant by addition of a compound which reacts with OH groups. The thickener is an aerogel of the oxides or hydrated oxides of Si, Ti, Al or Fe. The organic compound is an epoxy compound containing a terminal ethylene oxide group, or an organic isocyanate.

Greases

24. de Bataafsche, N. V., Dutch Pat. 75,308 (1954).

A grease is prepared by gelling a lube oil with an inorganic colloid, preferably a silicate, and at least 30% by wt. of a cationic, hydrophobic, surface active agent. Does not corrode steel and has improved emulsification properties.

25. Dilworth, P. J. and Roach, J. R., Oil Gas J., 54, 103 (1955). New Synthetic Grease Is Good Performer.

A new grease containing a combination soap-non-soap thickener and a nonsilicone synthetic oil will lubricate ball bearings over the temperature range - 65 to 450°F.

26. Hotten, B. W., U. S. Pat. 2,698,300 (1954).

Long chain mono-arylureas are used as gelling agents in lubricating greases.

27. Meyer, G. C. and Braendle, B. O., Inst. Spokesman, 18, 10 (1954), Estersils, A New Class of Thickening Agents.

The preparation and properties of non-soap greases prepared from Estersil are described.

28. Morway, A. J. and Mikeska, L. A., U. S. Pat. 2,694,683 (1954).

Lubricating greases having a high drop point and good stability can be prepared from thickeners (salts of pectic acid) and a mineral oil.

29. O'Halloran, Rosemary, U. S. Pat. 2,696,469 (1954).

Lubricating greases with extreme pressure properties are prepared from mineral oils, 1.5 to 10% aluminum soaps and 3 to 30% carbon blacks having a pH of 2.5, a particle size less than 20 and a volatile content of about 5%. The greases also contain 5-10% sulfurized sperm oil, 1-5% high molecular wt. fatty acid, and 0.1 - 2% tritolyl or tributyl phosphate.

30. Rogers, D. T. and Bartlett, J. H., U. S. Pat. 2,694,684 (1954).

Co-polymers of esters of unsaturated phosphonic acids with a polymerizable unsaturated ester such as Ac OCH:CH_2 are pour-point depressants and additives for fuels, lubricants and greases.

31. Armstrong, E. L., U. S. Pat. 2,704,363 (1955).

Lubricating greases of lower penetration and higher dropping points result if the greases are homogenized under pressure and the pressure is suddenly released.

32. Hotten, B. W., U. S. Pat. 2,709,157 (1955).

Sym. and unsym. N, N¹ - diacylphenylene diamines in which acyl groups contain 1-22 aliphatic carbon atoms are used as gelling agents in mineral oil.

33. Puddington, I. E. and Seriann, A. F., U. S. Pat. 2,714,091 (1955).

Hydrophilic, finely divided SiO_2 and a drying oil are added to a lube oil and the mixture heated to 100-150°C. Grease prepared in this manner have good water resistance.

34. Conner, Rex C., U. S. Pat. 2,706,715 (1955).

A low function grease is made of a mixture of 6-16% of a polymer of chlorotrifluoroethylene, M. P. 380-410°F, and a liquid polymer of the same monomer.

35. Brandle, Richard O., U. S. Pat. 2,746,922 (1956).

The rheological properties of a lubricating grease made from oils thickened with Estersil are controlled by adding 0.1 to 8.5% of a H-bonding electron donor. By addition of water, ethylene glycol or glycerol a lub. grease is formed which has a more constant consistency under humid storage conditions.

36. Peterson, W. H., Accinelli, J. B. and Bondi, A., Lubrication Engr. 12, 95 (1956). Nature and Performance of Some Inorganic Base Greases.

Greases gelled with silica and clay were shown to be superior to conventional soap greases with respect to water resistance, high temperature use and resistance to water. Careful adjustment of the fraction of the gel surface with surfact was important.

Miscellaneous

37. Coehen, C. B. and Umer, R. S., Petroleum Refiner, 33, 212 (1954), New Analysis for Complex Greases.

Emission spectrography, the observation of change on treatment with solvents, determination of saponification and acid number, color, odor and consistency are recommended for preliminary inspection of complicated greases. The following procedure was successful in separating the component of several greases: solvent partition chromatography and centrifugation.

38. Higgins, E. M., NLGI Spokesman, 19, 8 (1955), Correlations of ASTM Grease Worker Tests With Field Performance.

The ASTM grease worker test correlates with grease consistency behavior in overfilled housings but is unapplicable in many other applications.

39. McGrogan, John F., NLGI Spokesman, 19, 22 (1955), Mechanical Stability of Lubricating Greases.

A number of factors such as rate of shear, time exposure to shear, temperature and the presence of water or air affect the mechanical stability of greases.

40. Musselmann, J. M., NLGI Spokesman, 19, 11 (1955),
Correlation of Laboratory Tests with the Stability of Greases in
Freight Car Roller Bearings.

Mechanical stability of non-soap greases was measured with an ASTM grease worker shell rod roller tester and a test installation of a freight car roller bearing. No correlation was found between the standard laboratory tests and the roller bearing test.

41. Pearson, J. W., J. Inst. Petroleum, 41, 290 (1955).
Evaluation of Greases for Ball and Roller Bearings at Low Temperatures.

An apparatus was developed for low temperature studies of grease at constant shear stress or constant rate of shear.

42. Watson, F. J., Lubrication Eng., 11, 86 (1955), Small
Scale Evaluation on Synthetic Lubricants.

Oxidation, corrosion, flammability and thermal stability tests of greases are described.