

WADC TECHNICAL REPORT 55-240

PART II

ASTIA DOCUMENT No. AD 97282

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

*JOHN J. CHESSICK
ALBERT C. ZETTLEMOYER*

LEHIGH UNIVERSITY

SEPTEMBER 1956

MATERIALS LABORATORY
CONTRACT No. AF 33(616)-2440
PROJECT No. 3044

WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Carpenter Litho & Prtg. Co., Springfield, O.
400 - November 1956

Contrails

FOREWORD

This report was prepared by the Lehigh Institute of Research under USAF Contract No. AF 33(616)-2440. This contract was initiated under Project 3044, "Aviation Lubricants", Task No. 73310, "Aircraft Lubricating Greases", and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Lt. Donald Kjerland acting as project engineer.

This report covers work conducted from April 1955 to April 1956.

WADC TR 55-240 Part II

Contracts
ABSTRACT

Physical properties of several oils and surface characteristics of a variety of thickening agents were measured in order to index the nature and extent of the vehicle-thickener interface in non-soap grease dispersions. These properties of the oils and solids were correlated with the behavior of grease systems formulated from them. Modification of the interfacial region by water and polar organic additives was also investigated.

The combined results of these studies have led to some interesting conclusions regarding the mechanism of flocculation with consequent gel formation of polar and nonpolar solids dispersed in grease vehicles. The relatively low area polar solids used in this work require the presence of small amounts of water in the grease system for flocculation to occur in nonpolar vehicles. These polar solids, at least in the quantities used in this work, would not be effective thickeners in pure liquids or in liquids which dissolve or are miscible with large quantities of water. On the other hand, the nonpolar thickeners when dispersed in a vehicle do not need water to flocculate into a gel structure. These nonpolar materials were shown to be effective thickeners in both polar and nonpolar liquids. A proposed mechanism to explain the flocculation of these solids is based on the reduction in free surface energy brought about by the flocculation.

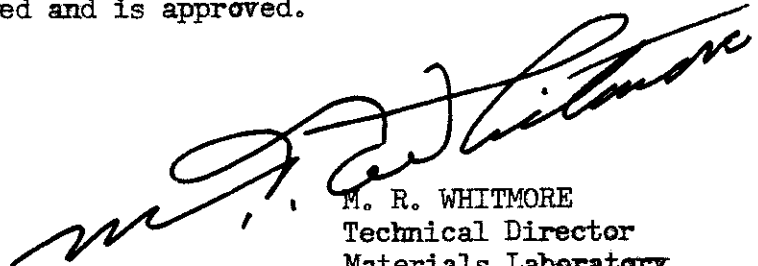
In addition, the mechanism of additive action has been explained qualitatively in terms of the mechanism of flocculation of these solids in the simple grease systems.

A variety of experimental approaches were used to gain a better understanding of grease structure. These included electrokinetic and conductance measurements and low angle X-ray scattering. X-ray scattering techniques have proved to be the most rewarding; indeed, marked diffraction maxima have been found corresponding to spacings of the order of 100 to 2000 Å units for copper phthalocyanine thickened greases.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

Contrails
TABLE OF CONTENTS

	Page
Introduction	1
I. THE GELLING OF ORGANIC LIQUIDS BY SOLIDS	3
Hydrophilic Thickeners in Organic Liquids	3
Hydrophobic Thickeners in Organic Liquids	15
II. THE INFLUENCE OF ADDITIVES ON TWO COMPONENT GREASE SYSTEMS	19
Grease Systems Containing Hydrophilic Thickeners	19
Grease Systems Containing Hydrophobic Thickeners	28
III. FUNDAMENTAL STUDIES OF NON-SOAP GREASE STRUCTURE	33
Electrokinetic Measurements of Non-Soap Greases	33
Conductance Measurements of Non-Soap Greases	33
Exploratory Low Angle X-Ray Scattering Studies	34
BIBLIOGRAPHY	36
APPENDIX A - Evaluation of the Gardner Mobilometer for Use in Measuring the Consistency of Greases	37
APPENDIX B - Surface Characteristics of Thickening Agents	41
APPENDIX C - Physical Properties of Oils	42

Contrails
LIST OF ILLUSTRATIONS

Figure	Description	Page
1.	Flocculation of Two Particles Under the Influence of Adsorbed Water	8
2.	Penetration of an Aerosil-Flexol 201 Grease as a Function of Additive Concentration . .	13
3.	Influence of Additives on Aerosil-Paraffin Oil Greases	20
4.	Influence of Additives at High Concentration on the Consistency of an Aerosil-Paraffin Oil Grease .	22
5.	Influence of Additives on an Aerosil-Flexol 201 Grease	24
6.	Influence of Additives at High Concentration on an Aerosil-Flexol 201 Grease	25
7.	Influence of Additives on a HiSil-Paraffin Oil Grease	26
8.	Influence of Additives on a HiSil-Flexol 201 Grease	27
9.	Influence of Additives on a HiSil-Ucon Adipate and a HiSil-MLO 8200 Grease Systems	29
10.	Influence of Additives on a Rutile-Paraffin Oil Grease	30
11.	Influence of Additives on an Estersil-Paraffin Oil Grease	31
12.	Typical Mobilometer Data	38
13.	Comparison of Mobilometer and Penetrometer Data . .	39

Contrails
LIST OF TABLES

Table	Page
I. Penetration Readings for Aerosil-Organic Liquid Dispersions	3
II. Penetrometer Readings for Aerosil-Organic Liquid Dispersions	4
III. Penetrometer Readings for Aerosil-Organic Liquid Dispersions	4
IV. Gelling of Organic Liquids by TiO_2	5
V. Setting Volumes of TiO_2 in Organic Liquids	6
VI. Sedimentation Volumes of 15.2 Micron Glass Spheres in Organic Liquids	9
VII. Thickening Ability of Solids in Paraffin Oil	12
VIII. Penetration Readings for Estersil-Organic Liquid Dispersions	16
IX. Properties of Greases on the Addition of Water, P_2O_5 or Organic Additives.	16
X. Heats of Wetting of Aerosil in Pure Liquids and Solutions	23
XI. Specific Conductance of Aerosil-Paraffin Oil Greases	34

The main objectives of this project are to investigate the fundamental factors involved in the formation of non-soap lubricating greases and to determine the relation of certain of these factors to the thermal, chemical and mechanical stability of non-soap greases.

Since gelling action in non-soap greases is primarily the result of interfacial phenomena, the study of the basic factors in their formation and stability falls properly into the realm of surface and colloid chemistry. Consequently, the research approach to the fundamental study has been divided into the following phases:

Characterization of grease thickeners on the basis of measured surface properties.

Characterization of a series of grease vehicles.

Measurement of the properties of simple dispersions of these solids and vehicles. Correlation of the measured properties with the properties of the single components.

A study of the important influence of water present in these simple solid-vehicle dispersions.

Studies of more complex grease systems containing the characterized solids and vehicles as well as simple additives, and the influence of water on these more complex systems.

Studies of grease structure.

During this report period efforts have been directed mainly toward an understanding of the mechanism of flocculation of polar and nonpolar solids in simple grease systems. In addition, studies of the influence of additives, which include water and straight chain heptyl derivatives, on the consistencies of these simple grease systems have been extended. These efforts have been elucidating to the point where qualitative mechanisms for the flocculation of grease thickeners can now be made. Furthermore, speculation of the behavior of additives can also be made in terms of the simple model offered for the gelling or flocculating process.

The research project is now directed in part to the establishment of a more rigorous model which will allow more quantitative

Manuscript released by authors April 1956 for publication as a WADC Technical Report.

Contrails

treatments of the gel-forming phenomena. Low angle x-ray scattering is the tool currently being explored to yield a more intimate picture of grease structures. While this present phase of the work could be the most fruitful, it is the most difficult in which to make rapid progress.

I. GELLING OF ORGANIC LIQUIDS BY SOLIDS

In order to evaluate the factors responsible for the gelling of a liquid by a solid, gels were formulated from polar and nonpolar solids and a variety of short-chain, undried, organic liquids. The solid and vehicle were blended to a constant consistency in a Waring Blender which was capped tightly to prevent loss of the more volatile liquids employed.

Hydrophilic Thickeners in Organic Liquids.--The consistencies of Aerosil-organic liquid dispersions as indexed by the penetrometer are given in Tables I, II and III where the greases are arranged in order of increasing penetration. It was found that the chloride compounds were most readily gelled by Aerosil, followed in order by the hydrocarbons, esters, aldehydes, acids, amines and glycols. The branched chain compounds were thickened more easily than their straight chain counterparts. The very polar compounds, glycerol and water,

TABLE I

PENETRATION READINGS FOR AEROSIL-ORGANIC
LIQUID DISPERSIONS

(a)

10 grams Aerosil/100 ml. liquid

Liquid	Density	Mol Wt.	Moles	Penetration
polybutene	---	5,000	0.02	145
tetrachloroethane	1.600	167.9	0.95	180
carbon tetrachloride	1.595	153.8	1.037	191
n-butyl chloride	0.884	92.6	0.95	217
ethyl benzoate	---	---	---	218
toluene	0.866	92.1	0.94	222
isopropyl benzoate	1.016	164.2	0.614	228
n-hexyl ether	---	186.2	---	240
benzene	0.879	78.1	1.13	246
isocamyl acetate	0.870	130.2	0.67	247
tributyl amine	---	---	---	213
Too fluid for measurements				
dibutyl amine				
nitropropane				
n-butyl alcohol				
iso-butyl alcohol				
sec-butyl alcohol				
t-butyl alcohol				
n-butyl amine				
glycerol				
water				

(a) Surface area about 180m²/g.

TABLE II
PENETROMETER READINGS FOR AEROSIL-ORGANIC
LIQUID DISPERSIONS

15 grams Aerosil/100 ml. liquid

Liquid	Penetration
n-butyraldehyde	170
propionic acid	173
isopropyl benzoate	182
nitropropane	187
isoamyl acetate	212
n-butyl acetate	226
n-butyl amine	348
dibutyl amine	197
too fluid for readings	
n-butyl alcohol	
isobutyl alcohol	
sec-butyl alcohol	
glycerol	
water	

TABLE III

PENETROMETER READING FOR AEROSIL-ORGANIC
LIQUID DISPERSIONS

20 grams Aerosil/100 ml. liquid

Liquid	Penetration
t-butyl alcohol	214
too fluid for readings	
isobutyl alcohol	
sec-butyl alcohol	
n-butyl alcohol	

25 grams Aerosil/100 ml. liquid

sec-butyl alcohol	215
isobutyl alcohol	215
too fluid for readings	
n-butyl alcohol	

could not be thickened to gels even at solid concentrations up to 40 wt. %.

To help in the interpretation of the Aerosil-organic vehicle data more information was obtained on the gelling ability of a more polar solid, titanium dioxide, and a nonpolar, hydrophobic thickener, Estersil. The thickening ability of TiO_2 in five undried organic liquids is illustrated qualitatively in Table IV. At first glance it appears that the liquid with the largest dipole moment was most easily gelled by TiO_2 . Closer inspection, however, reveals that the data for TiO_2 agreed well with the data for similar Aerosil-organic systems; but in these earlier more extensive studies polarity of the liquid did not always correlate with ease of gel formation. For example, the nonpolar hydrocarbon liquids were among the vehicles which gelled most readily. Factors other than dipole moment must be sought to explain the phenomenon of gel formation.

TABLE IV. (a)

GELLING OF ORGANIC LIQUIDS BY TiO_2 (MP-997) ^(b)		
Liquid (50 ml.) (decreasing dipole moments)	Solid wt. (g)	Condition of gel
nitropropane	15	begins to thicken
butyl chloride	15	begins to thicken
butyraldehyde	20	considerably thickened
butyl alcohol	20	begins to thicken
butyl amine	20	fluid

(a) TiO_2 (MP-997) was obtained from the National Lead Co., Titanium Division, South Amboy, N. J.

(b) Surface area about $105 \text{ m}^2/\text{g}$.

To help determine which parameters govern the formation of a gel, the literature was searched for pertinent and related data. Now it is fairly well recognized that flocculation of a dispersed solid in a vehicle is responsible for the physical properties of the dispersion. A qualitative measure of flocculation is believed to be obtained from studies of sedimentation rates and volumes of solids dispersed in liquids -- the more highly flocculated particles settle most rapidly and form the largest volume of sediment. Consequently, information on sedimentation volumes was selected for comparison with data on the gelling ability of solids dispersed in similar liquids. The data of Ryan et al. (1) for the sedimentation volumes of TiO_2 dispersed in a variety of organic liquids are given in Table V. The techniques employed by these workers in obtaining their data were insufficiently rigorous to insure completely dry systems. It is interesting to note

SETTLING VOLUMES OF TiO_2 IN ORGANIC LIQUIDS

Liquid	Settling Volume c.c.	Dipole Moment ^(a) E.S.U. x 10^{18}	Gelling Ability of Aerosil ^(b)
water	5.1	1.87	1
ethylene glycol	5.1		1
aniline	5.1	1.6	
heptyl aldehyde	6.9		
ethanol	7.1	1.7	2
n-propanol	7.1	1.7	2
butyric acid	7.1	1.7	3
acetone	8.5	2.7	
ethyl acetate	8.5	1.8	3
ethyl butyrate	8.7		
diethyl ether	12.8		
nitrobenzene	13.4	3.9	
butyric nitrile	13.9		
n-heptane	14.3		4
chlorobenze	15.1		
carbon tetrachloride	15.1	0	5
benzene	15.6	0	

(a) After C.R. Bloomquist and R.S. Schutt, Ind. Eng. Chem., 32, 827 (1940)
 (b) 1 indicates most difficult to gel, 2 next most difficult (etc.)

a similarity between the results of this work on sedimentation volumes and the data on the gelling properties of Aerosil and TiO_2 . These types of vehicles most difficult to thicken also have low sedimentation volumes with the polar solid. Ryan and co-workers correlated their results qualitatively with the polarity of the liquids employed. The dipole moments of the liquids included in Table V show that this correlation is not better than qualitative.

As pointed out, the data on gelling properties of polar solids compared favorably with that for sedimentation volumes in the same or similar vehicles. It is important to note that neither gel properties nor sedimentation volumes were measured for completely dry systems. On the other hand, evidence exists to show that sedimentation volumes of polar solids become the same or nearly so when dispersed systems are anhydrous. Actually, further data of Ryan and co-workers (1) show markedly less differences in sedimentation volumes as the drying conditions become more stringent. Furthermore, Galley and Puddington (2) noted that when rigorously dried solids such as starch, magnesium oxide, ferric oxide and talc were studied in dry liquids the final volume was only slightly affected by the liquid. Bloomquist and Schutt (3) also found that the sedimentation volumes of dry glass spheres in a series of different liquids were very nearly

the same if anhydrous conditions were employed. On the basis of this evidence from sedimentation volume experiments, and assuming a close relationship between these values and the values for the gelling ability of polar solids in similar vehicles, the obvious conclusion is reached that for completely dry systems very nearly the same amount of a given polar solid is required to produce a grease of a given consistency irrespective of the chemical nature of the vehicle. Any small difference in required amounts would result from small expected differences in lyospheres about the particles. It is important to note, however, that sedimentation data have been obtained only for relatively low area, polar solids. This point will be discussed below.

Striking evidence for the important influence of water dissolved in the vehicle is presented in Table VI where sedimentation volumes of dried glass spheres in systems with different water content are tabulated. Water increased sedimentation volumes and hence flocculation by some mechanism which must now be examined.

Kruyt and van Selms (4) studied the flow behavior of suspensions of quartz in a nonpolar oil of the same density ($C_2H_2Br_4-C_2H_2Cl_4$) with additions of small amounts of water. They found an increase in yield stress with water content of the system. In addition, these workers pointed out that the viscosity of the system (wet) is not much greater than that of the dispersed (dry) systems of the same concentration of solid once it has been made to flow. They postulate first adsorption of water on the surface of the polar solid which creates a water/oil interface. This water/oil interface is decreased by coalescence of the water layers on adjacent particles according to Figure 1. This mechanism of flocculation of solids in the absence of electrokinetic effects does not seem unreasonable. In fact much data have already been presented in previous Air Force reports from this Laboratory concerning the remarkable influence of water on the consistencies of greases -- particularly with polar solids dispersed in non-polar vehicles. Consequently, since this proposed mechanism is dependent on the adsorption of water from solution, the parameters which govern solution adsorption should be the important ones in the formation of the gel structure of these non-soap greases. These parameters then for a solid-water-organic vehicle system, assuming there is enough solid initially present to form a continuous internal structure, are:

1. Temperature.
2. Increase in concentration of solid above the minimum value required to give a continuous gel structure.
3. Relative concentration, or more accurately the activity, of the water dissolved in the vehicle.
4. The free energy change on adsorption onto the surface of the thickener particles.
5. The free energy change on coalescence or flocculation of particles.

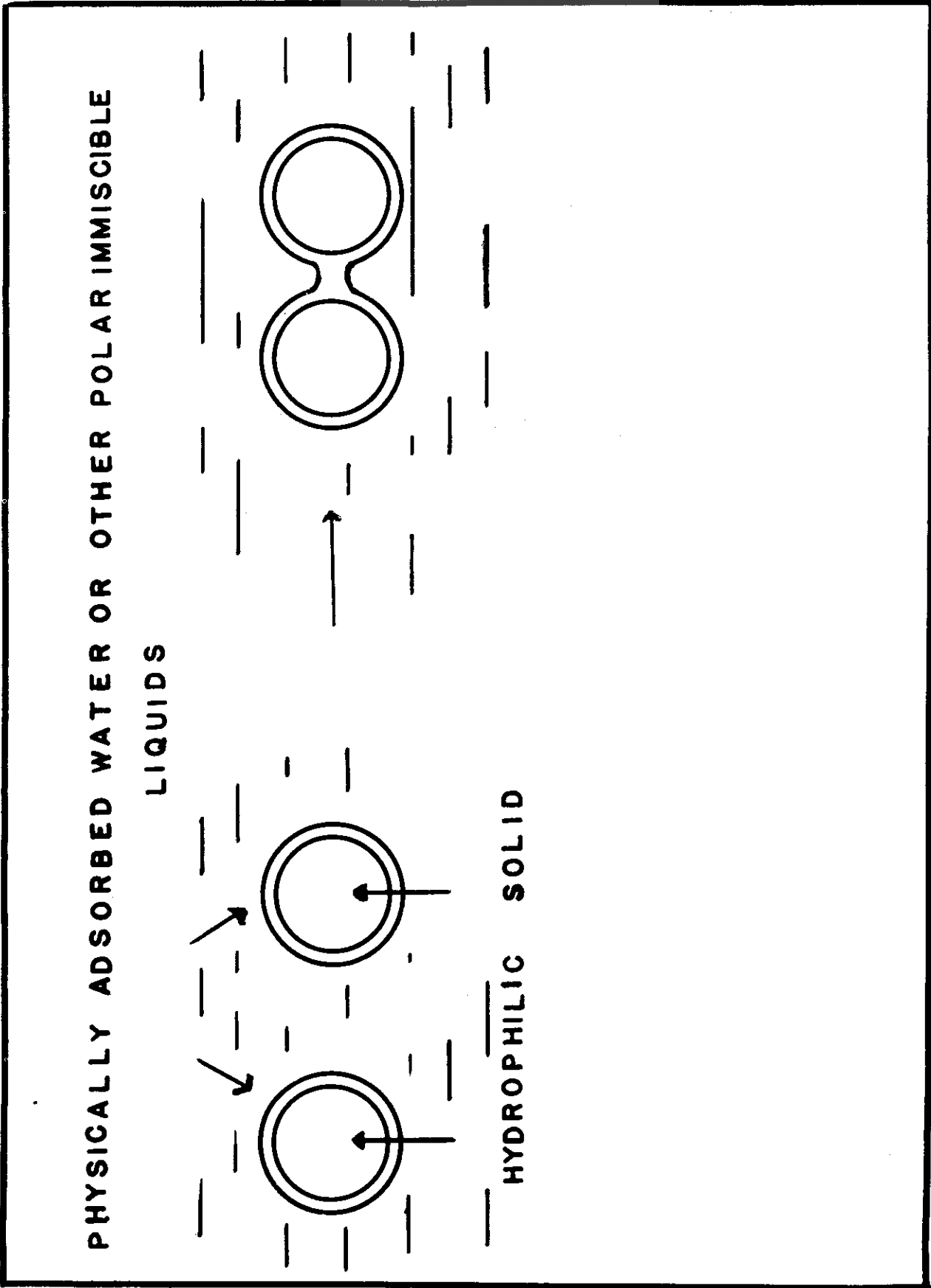


Figure 1. Flocculation of Two Particles Under the Influence of Adsorbed Water

Contrails
TABLE VI.

SEDIMENTATION VOLUMES OF 15.2 MICRON
GLASS SPHERES IN ORGANIC LIQUIDS (ml./g.)^b

	In Water Sat'd Liquids	Liquids from Freshly Opened Bottles	Pure Liquids
water			0.73
ethyl alcohol			0.75
acetone			0.73
n-propyl alcohol			0.73
n-butyl alcohol	1.67	0.78	0.75
benzyl alcohol	2.20	0.78	0.79
amyl alcohol	2.55	0.75	0.75
ethyl acetate	2.00	0.85	0.85 ^a
aniline	1.50	0.74	0.75
nitrobenzene	2.80	0.78	0.75
benzene	2.73	1.18	0.79
CCl ₄	3.20	2.77	0.95 ^a
toluene	3.55	1.88	

(a) Ultimate Dryness not reached

(b) After C.R. Bloomquist and R.S. Schutt, Ind. Eng. Chem., 32, 827 (1940)

A consideration of these parameters allows at least qualitative predictions, at this time, concerning the behavior of a polar solid dispersed in an organic liquid. Accordingly, in the complete absence of water, the flocculation of a solid in a pure liquid would be solely a function of the concentration and particle diameter of the solid. Consequently, flocculation might be expected to be small because of the small areas of contact between particles as a consequence of the molecular irregularities present on most surfaces. The polar nature of the solid and vehicle determine whether water will be preferentially adsorbed on the surface to aid flocculation; or whether, mixed adsorption of water and vehicle will occur. The solubility of water in the grease vehicle is important since the relative concentration of water, i.e., the amount of water present divided by the solubility of the water under conditions of measurement, is the most important single factor determining the amount of water available for surface adsorption and consequent flocculation. For example, if an undried solid is dispersed in a dry vehicle which dissolves only small quantities of water, most of the water on the solid surface will remain there rather than go into solution.

Heat of solution values are also important because they can indicate qualitatively the strength of interaction between vehicle and

Contrails

dissolved water and thus provide a measure of the ease with which water can be adsorbed from solution into the solid surface. Temperature and its relationship to solubility of water in the vehicle and adsorption on the solid is important particularly where high temperature operating conditions are met.

Application of these concepts is extremely difficult because sedimentation volume and gelling data for solids in vehicles exist only for dispersions that contain unknown amounts of water. Ideally, these data should be collected for samples with identical equilibrium, relative concentrations of water in the vehicle. For example, an equilibrium relative concentration of about 0.15 would be quite suitable since the mass of available adsorption data indicate that at this concentration a polar solid will be covered with about a monomolecular film of adsorbed water in the absence of mixed adsorption. With polar vehicles this arbitrary equilibrium concentration might be of little use because of mixed adsorption. Nevertheless, the data presented in Table V does show increases in sedimentation volumes for vehicles of low water solubility and high interfacial tension measured against water regardless of the polarity of the vehicle. Certainly, this interesting and important technical area deserves much more attention. The practical significance of further findings here would be great.

On the basis of the results obtained thus far there is little doubt that water plays an important role in the formation of non-soap greases. There are, however, some important questions which remain to be answered. For example:

1. Do trace amounts of water influence flocculation of polar solids or is a monomolecular adsorbed water film necessary as might be inferred from Figure 1?
2. Will the polar solids used as grease thickeners in this investigation flocculate in a pure, nonpolar vehicle or is the presence of water necessary? If not, why not? What is the relative importance of particle diameter, particle surface irregularity and particle surface energy in the flocculation process.
3. Do clean, dry solids flocculate by particle to particle contact or are the forces of attraction propagated through the liquid? How important is the lyosphere?

Answers to these questions were sought in the studies described below.

On the basis of available data, polar solids have been judged far more effective grease thickeners than their hydrophobic counterparts (6). These studies were conducted with dry solids. The vehicles, nonpolar generally, were not dried and contained small amounts of dissolved water. Whether the greater thickening ability of

the polar solids resulted from greater solid surface-vehicle interaction, (lysosphere), a high interfacial energy between liquid and solid, or from the influence of these trace amounts of dissolved water acting as a flocculating agent had not been determined. Studies have now been conducted with the polar solid Santocel 54 in Flexol 201 under increasingly anhydrous conditions.

Dispersions containing 14 wt. % Santocel 54, a polar silica, in Flexol 201 gave a micropenetrometer reading of 160; neither the solid nor the vehicle were dried. If the solid was dried at 100° for 4 days before dispersion into the undried vehicle, the micropenetrometer reading increased to about 200. No significant increase in penetration was found if, in addition to drying the solid at 100°F., the vehicle was also dried over P₂O₅ or MgSO₄. When drying techniques were used, the solid and vehicle were premixed by spatulation in a dry box containing P₂O₅. Unfortunately, this premix had to be milled under the usual atmospheric conditions; hence, it is extremely unlikely that a completely water-free grease was prepared despite the stringent drying conditions initially employed. Therefore these findings, although inconclusive, indicated that if water was responsible for flocculation and consequent gel formation in these polar solid-nonpolar vehicle systems, then only trace amounts (probably not even monomolecular films) of adsorbed water were necessary. A significant confirmation that trace amounts of water play an important role in the formation of grease structure was found by adding small amounts of P₂O₅ by spatula into well-dried greases whereby a marked breakdown in structure occurred. These dispersions became too fluid for penetrometer measurements; when exposed to atmospheric conditions, the gel structure returned on standing. Anhydrous MgSO₄ also caused breakdown in gel structure and for periods of several weeks even if the grease was exposed to atmospheric conditions. The most likely explanation is that the drying agents combined chemically with the trace amounts of water available for flocculation. Thus, it appears obvious that 14 wt. % Santocel 54 is an insufficient quantity of solid to form a gel with Flexol 201 in the complete absence of water.

The P₂O₅ desiccant also fluidized greases containing the other polar solids, Aerosil and HiSil. On the other hand, P₂O₅ does not affect the consistency of greases containing the hydrophobic thickeners, Estersil and the carbon blacks.

Table VIII gives an indication of the average wt. % solids used in the past to prepare greases. Estersil and Carbolac 2, both hydrophobic thickeners, were included for comparison. Only about 12 wt. % of the polar Aerosil was necessary to form a grease of penetration 176, whereas 15 wt. % of Estersil was required to form a grease of penetration 231 even though the area of Estersil is nearly twice

THICKENING ABILITY OF SOLIDS IN PARAFFIN OIL

Solid	Area (m. ² /g.)	Heat of Immersion in H ₂ O (ergs/cm. ²)	Wt. % solid	Penetration
Aerosil	140-180	154-180	~ 12	176
HiSil	129	460	17	158
Rutile	~ 80	-	25	183
Estersil	290-300	~ 10	15	231
Carbolac 2	660-700	90	~ 10	224

that of Aerosil. On the basis of such evidence accumulated in the past, hydrophilic solids were judged to be much more effective thickeners than hydrophobic solids. This finding suggested that the surface energy of the solid was far more important than the extent of solid-vehicle interface when comparing these two types of solids. In light of the new evidence found for the influence of water on the flocculation of polar solids, it appears obvious that this comparison is unreasonable, and that the thickening ability of polar and nonpolar solids might not be so radically different if they were dispersed in pure liquid or in liquids where the influence of water would be small.

The evidence presented thus far suggested that the formation of a grease in nonpolar vehicles containing small amounts of water was possible with much smaller quantities of a dry polar solid than if the liquid was water free. In addition, the consistency of the grease containing the polar solid increased markedly as the water content of the systems was increased. The formation of structure by trace amounts of water requires bridges made up of small quantities of water - perhaps, even a few molecules per bridge between the solid particles. Certainly in the very stringently dried systems only fractional water layers, far below a monolayer, could have been adsorbed. This mechanism, of course, requires mobility of adsorbed surface water molecules to junction points between particles. Above monolayer coverages, the high interfacial tension between the adsorbed water-oil interface would be reduced markedly by coalescence of water covered particles as illustrated in Figure 1.

It is interesting to note that another immiscible liquid besides water has been found to cause a sharp increase in consistency of a grease thickened with the polar solid, Aerosil. In Figure 2 the penetration measurements of Aerosil-Plexol 201 greases are plotted as a function of the wt. % ethylene glycol added. Evidently, here also flocculation is increased as the concentration of ethylene glycol is increased due to coalescence of particles and the reduction of

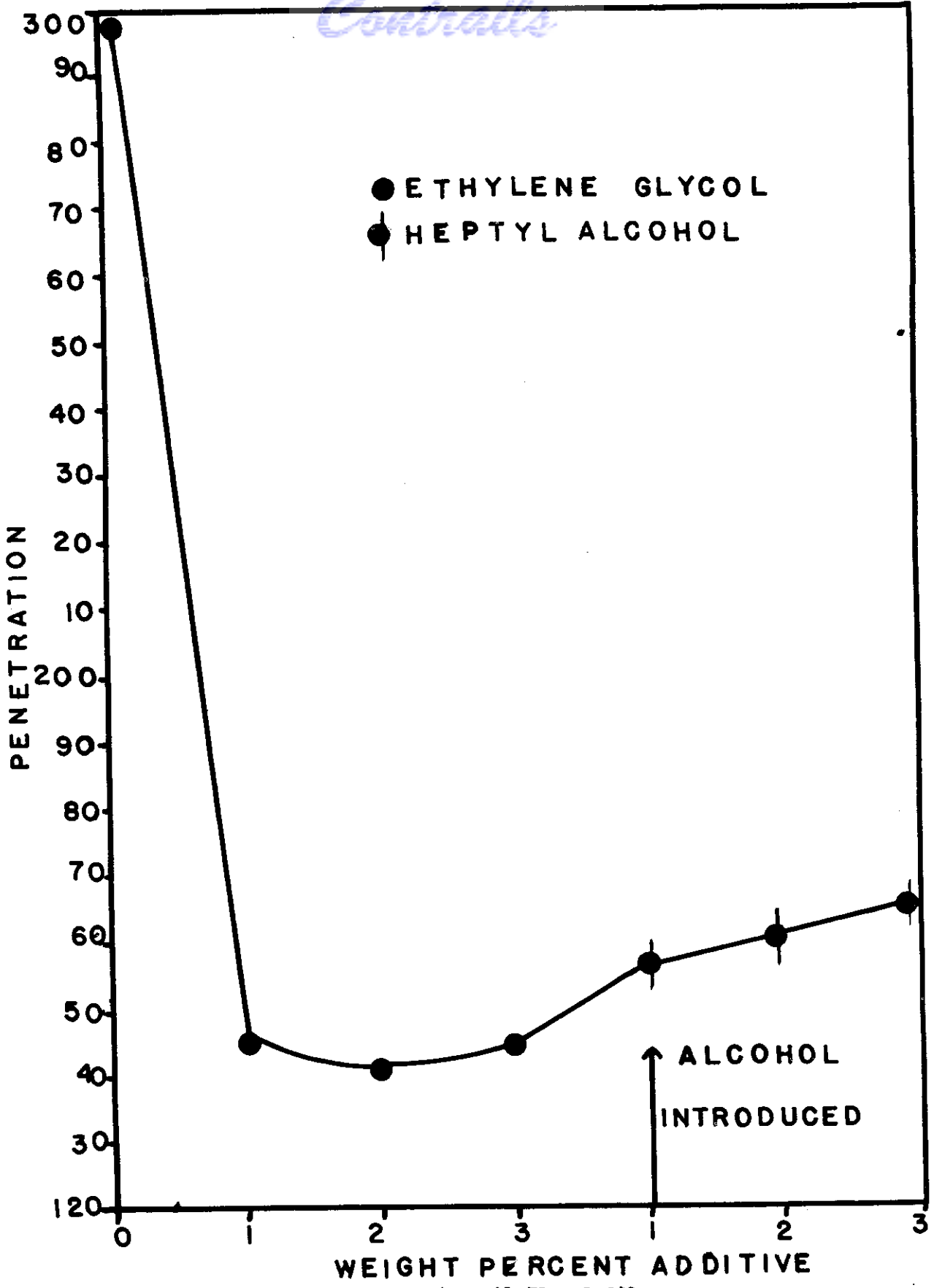


Figure 2. Penetration of an Aerosil-Flexol 201 Grease as a Function of Additive Concentration

interfacial tension between adsorbed ethylene glycol and the vehicle. Undoubtedly, other immiscible liquids with high interfacial tensions measured against the vehicle, and which are preferentially adsorbed by the solid, could cause flocculation by this same mechanism. It is suggested that low molecular weight amines, alcohols, acids, aldehydes, etc., might thicken greases formulated with polar solids in nonpolar vehicles in direct contrast to the more usual thinning effect of the heptyl compounds previously studied extensively. Low molecular weight, difunctional organic compounds should be particularly effective thickening agents. These ideas will be tested.

The effect of a thinning agent heptyl alcohol, on the consistency of the glycol-Aerosil-Flexol grease is also illustrated in Figure 2. The significance of this effect will be discussed in a following section where more complex systems will be treated.

More evidence has been found to support the suggestion that water is an important flocculating agent in certain systems. If water is important for the flocculation of polar solids, its influence would be greatest in nonpolar vehicles (like common grease vehicles) and least in polar vehicles (like ethylene glycol). That is, a given quantity of water is more available for adsorption in a nonpolar vehicle which dissolves only small quantities. Secondly, in nonpolar vehicles the water is preferentially adsorbed by the solid producing an extensive interface between the immiscible adsorbed water and the vehicle. This interface is absent in pure water or even in water containing polar vehicles like ethylene glycol; consequently, in such cases flocculation by coalescence of film-covered particles according to the mechanism illustrated in Figure 1 is impossible. Experimentally, it was found that 10 to 15 wt. % Aerosil or HiSil (amounts sufficient to form a grease with nonpolar vehicles) do not gel undried ethylene glycol. In fact, amounts as high as 50 wt. % and higher are still ineffective; good evidence was thus developed that water is a necessary flocculating agent for these relatively low area, polar solids.

In contrast, normal amounts of a carbon black (XC-72) and Estersil form greases as effectively with ethylene glycol as with the usual grease vehicles.

These results partly answer the questions posed in the preceding section. Water does indeed play an important role in the flocculation of the polar solids in nonpolar vehicles. Even trace amounts of water, i.e. fractions of an adsorbed monolayer, evidently can cause flocculation through the formation of water bridges between adjacent particles. At large water contents, flocculation results by coalescence of water covered particles with consequent decrease in the interfacial energy between the immiscible adsorbed water film and the

nonpolar vehicle. The evidence suggests, also, that the polar solids whose surface areas range from about 120 to 170 m²/g. used as grease thickeners in this work cannot effectively thicken a pure grease vehicle in the complete absence of water. Evidently, particle to particle interaction is not sufficiently pronounced with polar solids of these areas to lead to significant gel formation. It is not known whether dry polar solids of much smaller particle diameter can effectively gel pure liquids at reasonable concentrations.

The difficulties in directly preparing completely anhydrous greases prevents the measurement of the influence of the chemical nature of the liquid on the gelling ability of polar solids. However, the sedimentation volume data collected from the literature for systems studied under anhydrous conditions reveals this influence to be small or negligible. This, of course, implies that the effect of the interfacial energy between solid and pure liquid, γ_{SL} , on flocculation is small. It must be remembered, however, that most of the sedimentation volume studies were carried out with low area polar solids -- 20 m²/g. or less and the behavior found with these materials might be quite different than for solids of very high surface areas.

Hydrophobic Thickeners in Organic Liquids. -- The gelling ability of the hydrophobic thickener, Estersil, was measured in a limited number of organic liquids. As expected, the differences in the thickening action of Estersil in the various liquids was small compared to polar solids as shown in Table VIII. However, Estersil thickens butyl alcohol less effectively than it thickens butyl chloride. It may be significant that heptyl alcohol when used as an additive in an Estersil-paraffin oil grease caused large decreases in consistency whereas heptyl chloride had little effect. It is likely that the alcohols adsorbed preferentially onto the surface of Estersil making the surface even more hydrophobic and less effective as a thickening agent. These results, however, indicated that if water played a role in gel formation with Estersil, it was a minor role.

There is good evidence to suggest that of the solids used in this investigation, the polar solids flocculate to form a grease gel differently than do the nonpolar solids. Some of the properties of greases containing these solids which illustrate this difference are listed in Table IX. First, the hydrophobic thickeners had much greater surface areas. Secondly, trace amounts of water did not influence the flocculation process of hydrophobic thickeners. Moreover, the addition of P₂O₅ did not affect the consistency of greases made with these solids. Relatively large quantities of water also had little or no effect on the consistencies of these greases. Furthermore, normal quantities of these nonpolar solids formed greases in either ethylene

PENETRATION READINGS FOR ESTERSIL-ORGANIC LIQUID DISPERSIONS

15 grams Estersil/75 ml, liquid

<u>Liquid</u>	<u>Penetration</u>
n-butyl chloride	200
n-heptane	226
benzene	226
toluene	230
tetrachloroethane	259
n-hexyl ether	272

20 grams Estersil/75 ml, liquid

iso-amyl acetate	231
butyl alcohol	240

TABLE IX

PROPERTIES OF GREASES ON THE ADDITION OF WATER, P₂O₅ OR
ORGANIC ADDITIVES

<u>Solids</u>	<u>Nonpolar Vehicles (a)</u>			<u>Polar Vehicles (b)</u>
	Effect on the Consistency of a Grease on Addition of Heptyl			
	H ₂ O	Additive	P ₂ O ₅	
carbon blacks (c) 250-1000 m ² /g.	no effect	little or no effect	no effect	forms grease
Estersil 300 m ² /g.	small effect	large effect	no effect	forms grease
Aerosil, HiSil 130-170 m ² /g.	large effect	large effect	large effect	no grease forms up to 50 wt. % solid

(a) Plexol 201, Paraffin Oil

(b) Ethylene glycol (undried)

(c) Of the numerous carbon blacks, only Mogul, Carbolac 2 and XC-71 were examined for these effects.

glycol or the nonpolar grease vehicles, a fact which again indicated the negligible influence of water on the development of structure with

these solids in non-soap greases. However, the consistencies of Estersil greases, like the greases containing polar solids, were strongly influenced by the organic, heptyl derivatives used as additives, but in a different manner. These additives did not influence the consistencies of carbon black-nonpolar vehicle greases.

What then is (or are) the mechanism(s) of flocculation of these homopolar solids in organic liquids? From the differences illustrated in Table IX, they are apparently not the same for Estersil as for the blacks; and therefore these solids will be treated separately. Estersil is a silica gel whose surface hydroxyls have been converted to -OR groups by treatment with primary or secondary alcohols. Although the material is hydrophobic and most difficult to wet by water, the surface is not completely covered by these silica ester groupings. Water and nitrogen measurements of Estersil have revealed that this material has hydrophilic surface sites which occupy the equivalent of 3.5% of the surface. This area represents the uncoated portions of the surface. Flocculation of Estersil may result, therefore, from an interlocking of the hydrocarbon groups of adjacent particles in the free space which exists on the surface of each, or by hydrogen bonding between unreacted hydroxyl groups on the surfaces of adjacent particles. Additives of the straight chain, heptyl type could decrease flocculation by adsorbing preferentially into these free, unesterified sites of the Estersil surface. It is interesting that the thinning effect of these additives on Estersil greases are not the same as for the silica (HiSil, Aerosil and Santocel) greases.

The mechanisms offered to explain the flocculation of Estersil certainly would not be completely appropriate to carbon black dispersions. Indeed, carbon blacks are quite different in behavior from all the other thickeners studied in that neither P_2O_5 , additives nor amounts of water up to 3 to 4 wt. % significantly alter the consistency of greases containing the blacks. Of course, McBain (7) pointed out that blacks adsorb organics most strongly from water or polar vehicles like glycol, much less from hydrocarbons. Hence, it is quite likely that in the carbon black greases studied here, the blacks are preferentially wet by the nonpolar (hydrocarbon like) vehicles. Surprisingly, the heptyl derivatives also had small effect on the consistency of a carbon black-ethylene glycol grease in concentrations up to 6 wt. %. It is interesting to note that the carbon blacks gel efficiently both polar and nonpolar vehicles.

The mechanism of flocculation by carbon black systems is not as yet quite clear and efforts are being made to learn more about this phenomenon. Theoretically, at least, a solid completely dispersed in a pure liquid would also tend to flocculate spontaneously since this process leads to a reduction in the interfacial free energy, γ_{SL} .

Conclusions

between the solid surface and pure liquid by an amount proportional to the area decrease on particle-particle contact. It appears unlikely, however, considering the molecular irregularity of most solid surfaces, that the decrease in area (and free energy) would be large. Certainly it appears that this mechanism is not important for the polar grease thickeners dispersed in ethylene glycol. Neither does it appear important for these same solids dispersed in nonpolar vehicles in the absence of water. Of course, flocculation by this mechanism could become more important as the surface area of the grease thickeners is increased or if a larger area of contact between particles is made possible. Smoother surfaces or anisotropic particles might prove more effective. For these reasons, carbon blacks may well flocculate by particle to particle contact and without the aid of water or any other flocculating agent unlike the polar solids used in these studies. These findings suggest that flocculation by particle to particle interaction is only possible when the dispersed solid particles have particle diameters below some critical value, although surface homogeneity must also be considered. Consequently, high area polar solids with areas of about 300 m²/g. might also be expected to gel pure liquids either polar or nonpolar. Efforts will be made to check this speculation if such high area polar solids can be obtained. Increased concentration of solid might also be important in bringing the effect of particle-particle contact into play although 30 wt. % samples of Aerosil did not gel ethylene glycol. This amount is more than three times greater than that required to form a grease with undried Plexol or paraffin oil. This comparison suggests again that particle diameter, not total solid-liquid interfacial tension, is important.

Some evidence exists to suggest that carbon black flocculation takes place by particle to particle contact. If flocculation occurs as a result of a decrease in interfacial energy, for carbon black dispersions, then the thickening ability of the blacks should be greatest in polar vehicles where flocculation would cause the greatest decrease in free energy. That this is so is indicated by the following results: The penetration of 10 wt. % black, XC-72, in glycol was 301; 12 wt. % black in the less polar Plexol 201 was 299.

II. INFLUENCE OF ADDITIVES ON TWO COMPONENT GREASE SYSTEMS

Preliminary work has already been carried out on the influence of grease additives on the formation and stability of non-soap greases (5). Originally, two contrasting types of gel systems were studied. These were formulated from paraffin oil with Aerosil, a polar solid, and Estersil, a nonpolar solid. The grease thickeners were dried before dispersion but the vehicles were not, and undoubtedly they contained small quantities of dissolved water. This dissolved water, as pointed out, is important in giving structure to greases containing the polar thickeners. The organic additives were all seven carbon, straight-chain compounds with a single functional group. The functional groups were selected to cover a wide range of dipole moments and represented functional groups encountered in the more common, but more complex grease additives.

Grease Systems Containing Hydrophilic Thickeners.--The following dry solids: Aerosil, HiSil, Rutile, Estersil and the Cabot carbon blacks, Carbolac 2, Mogul raw material and X-71, have now been studied in one or more of the following undried vehicles--paraffin oil, Plexol 201, MLO-8200 and Ucon Adipate 465.

It was found that small amounts of heptyl alcohol and heptyl amine considerably thinned Aerosil-paraffin oil greases and that at about 2 to 3 wt. % additive the systems became too fluid for penetrometer measurements. The other additives had a much smaller effect. The results of this study are summarized in Figure 3 where the penetration of the grease is plotted as a function of the percent additive.

The marked thinning action of the amine and alcohol could have resulted from a preferential adsorption of these compounds by Aerosil. The adsorbed organic film could then have sterically prevented the flocculation of particles by the water present in the system. Indeed, the drying agents, $MgSO_4$ and P_2O_5 , had the same effects on the consistencies of samples of this grease. In the same manner, limited adsorption in the additive concentration range studied could account for the small effects of the chloride, aldehyde and acid on the consistencies of Aerosil greases. However, limited adsorption implies a much higher solubility in the grease vehicle for these compounds. As previously pointed out, the relative concentration of the adsorbate should be one of the most important parameters governing adsorption from solution and that adsorption of a monolayer of additive might be expected to occur at about 0.1 to about 0.2 relative equilibrium concentration of additive. Consequently, if the concentration is increased enough, eventually a point should be reached where the amount adsorbed should be sufficient to impart complete stabilization

Controls

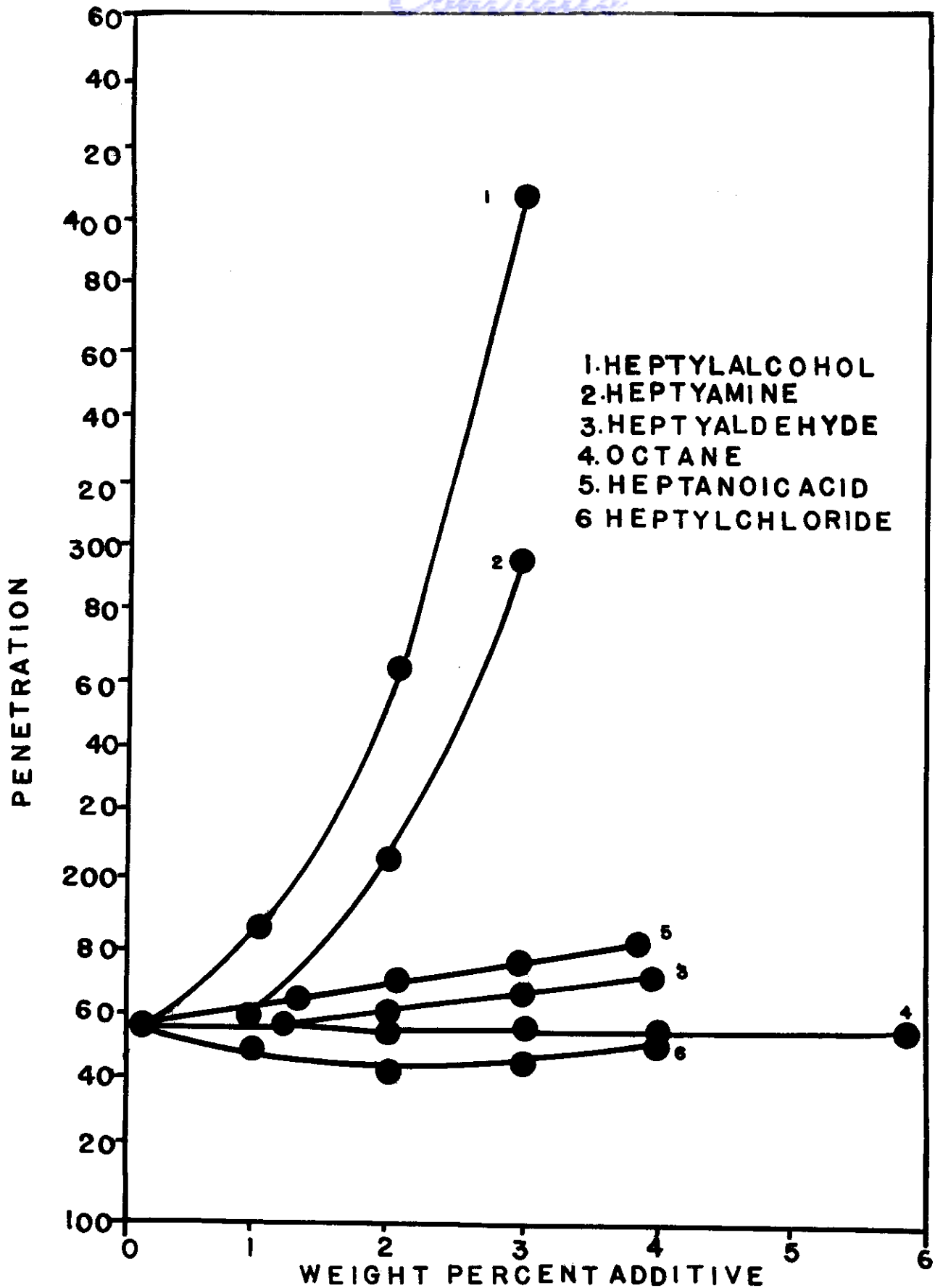


Figure 3. The Influence of Additives on Aerosil-Paraffin Oil Greases

Conclusions

(deflocculation) to the disperse phase and the marked thinning effect as noted with the amine and alcohol should occur. However, where the acid and chloride were studied at concentrations up to 10 wt. %, an abnormally high loading, no marked consistency changes were found as shown in Figure 4. These results do not support the adsorbed additive film concept unless the solubilities of the additives are abnormally high; this seems an unlikely possibility.

The possibility exists that specificity occurred during adsorption from solution and that the amine and alcohol were exclusively and possibly chemically adsorbed onto the silica surface. To establish these conjectures, numerous heats of wetting determinations were made for the immersion of several polar solids in pure organic liquids. Where only physical adsorption was involved, it was found that the interaction energy between the solid and liquid increased as the dipole moment of the wetting liquid increased. For this reason, it was expected as a first approximation that the interaction of the heptyl aldehyde, chloride or acid would be greater than that of the alcohol and amine when used as additives in the Aerosil-paraffin oil systems. Consequently, the compounds with the greater dipole moments were expected to be the more effective additives in these greases. Actually, the reverse was true: the alcohol and amine altered the consistencies of the greases most. It appeared then that the adsorption of the amine and alcohol by the silica surface was chemical in nature or that the vehicle altered the adsorption characteristics of these compounds so that they are more completely adsorbed when in solution than the more polar additives. To determine which mechanism was correct, heat of wetting measurements of Aerosil in additive type vehicles as well as in solutions of the additives in paraffin oil were measured. These data are shown in Table X. All measured heat values were much too low to be attributed to any but physical interactions. The values for the heats of immersion of Aerosil in the pure additive type liquids fell in the order expected from dipole moment considerations.

It is interesting to note that the heat of immersion of Aerosil in the paraffin oil solution of the chloride is less than the heat of immersion in pure paraffin oil and that the chloride was the only additive that thickened the grease. The highest heat value from solution was found for the amine solution. The amine additive, of course, had the most effect on grease consistency: 2 wt. % amine actually produced a grease too fluid for penetrometer readings. These measurements indicated that high heat of wetting values for solids immersed in the pure additive liquids do not necessarily mean high heats of adsorption from solution. Furthermore, the heat of immersion values in solutions of the additive appear to bear some relation to their influence on the consistency of the grease. However, the heat effect in these cases cannot be readily interpreted since the net heat includes a term for the dilution of the solution due to adsorption as well as the heat for the wetting of the surface.

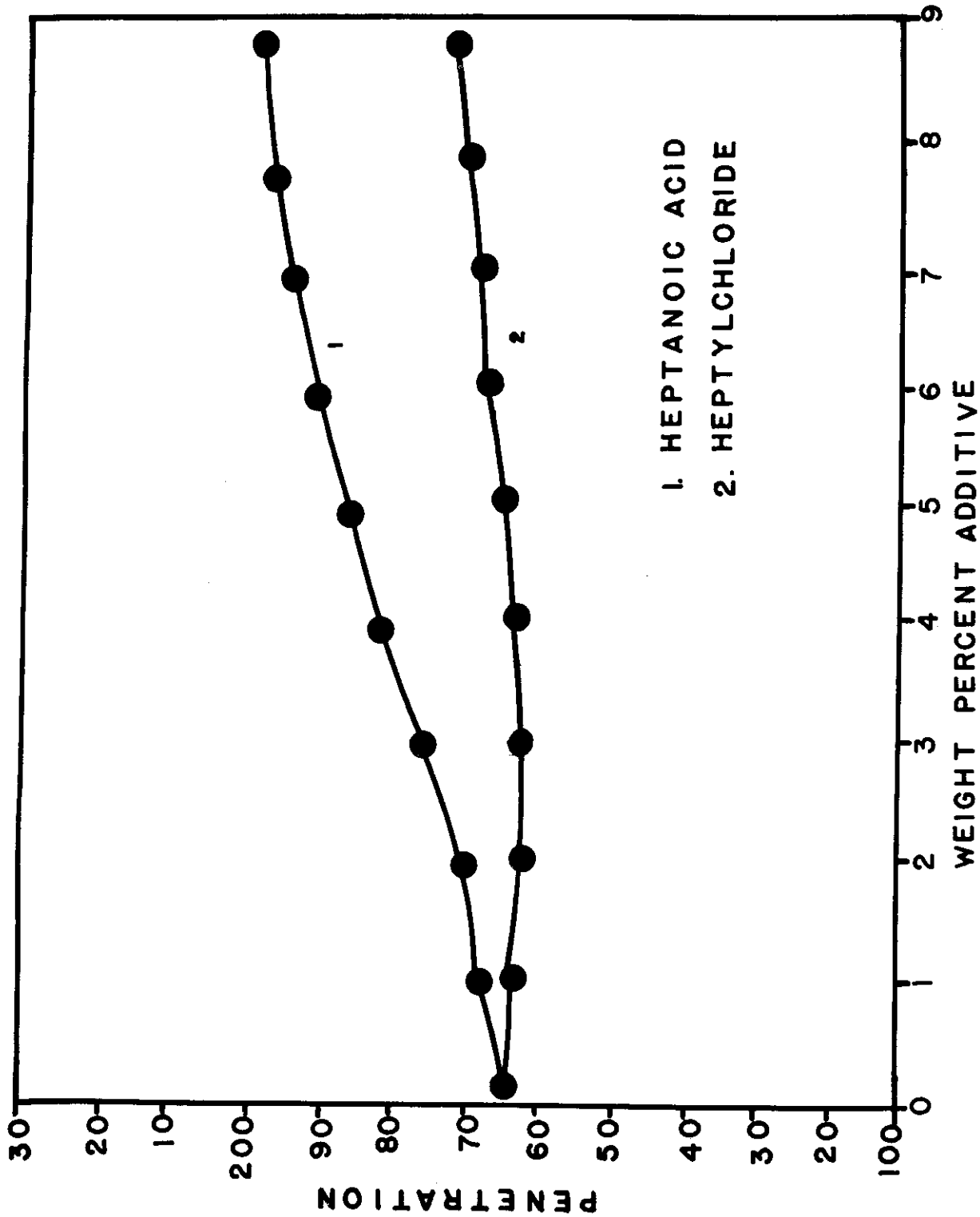


Figure 4. The Influence of Additives at High Concentrations on the Consistency of an Aerosil-Paraffin Oil Grease

HEATS OF WETTING OF AEROSIL IN PURE LIQUIDS AND SOLUTIONS

Liquid	Heat of Immersion ergs/cm. ²
water	180
plexol	170
paraffin oil	90
butyl chloride	212
butyl alcohol	161
paraffin oil + 3% heptyl chloride	70
paraffin oil + 3% heptanoic acid	120
paraffin oil + 3% heptyl alcohol	125
paraffin oil + 3% heptyl aldehyde	130
paraffin oil + 3% heptyl amine	210

An unlikely possibility is that another mechanism of additive action besides adsorption is operative. For example, the additive may hydrate in solution to tie up water which is normally effective in the flocculation and gel formation of the polar solid containing greases. However, it is rather difficult to understand why only the amine and alcohol, and not the acid, hydrate in this fashion. Certainly, further work is required to elucidate these findings.

From these heat of wetting measurements, it appeared that a grease vehicle altered the adsorption characteristics of additive compounds relative to their adsorption characteristics in the pure state. To study further the influence of the vehicle on additive behavior, Aerosil -- additive studies were carried out with another vehicle, Flexol 201. Data are shown in Figure 5 where the penetration of the grease is plotted as a function of the percent additive. It is at once evident that particularly at low additive concentration, the additives behave differently in Flexol 201 than in paraffin oil. However, at higher additive concentration the relative influence of these additives in Flexol 201 were similar to that found with these additives in paraffin oil. This point is illustrated in Figures 5 and 6. Figure 5 illustrates behavior at low additive concentration, and Figure 6 at high additive concentration.

The more polar silica HiSil, described in the Appendix, was selected for study in paraffin oil and in Flexol 201 to compare its behavior with Aerosil in these same vehicles. The heptyl derivatives behaved similarly in both these HiSil grease systems particularly at higher additive concentrations. Furthermore, additive influence on HiSil was similar to that found for Aerosil in these same vehicles but not at the same concentration of additives. For example, less amine or alcohol was required to thin the more polar HiSil greases. These results are shown in Figures 7 and 8.

Contrails

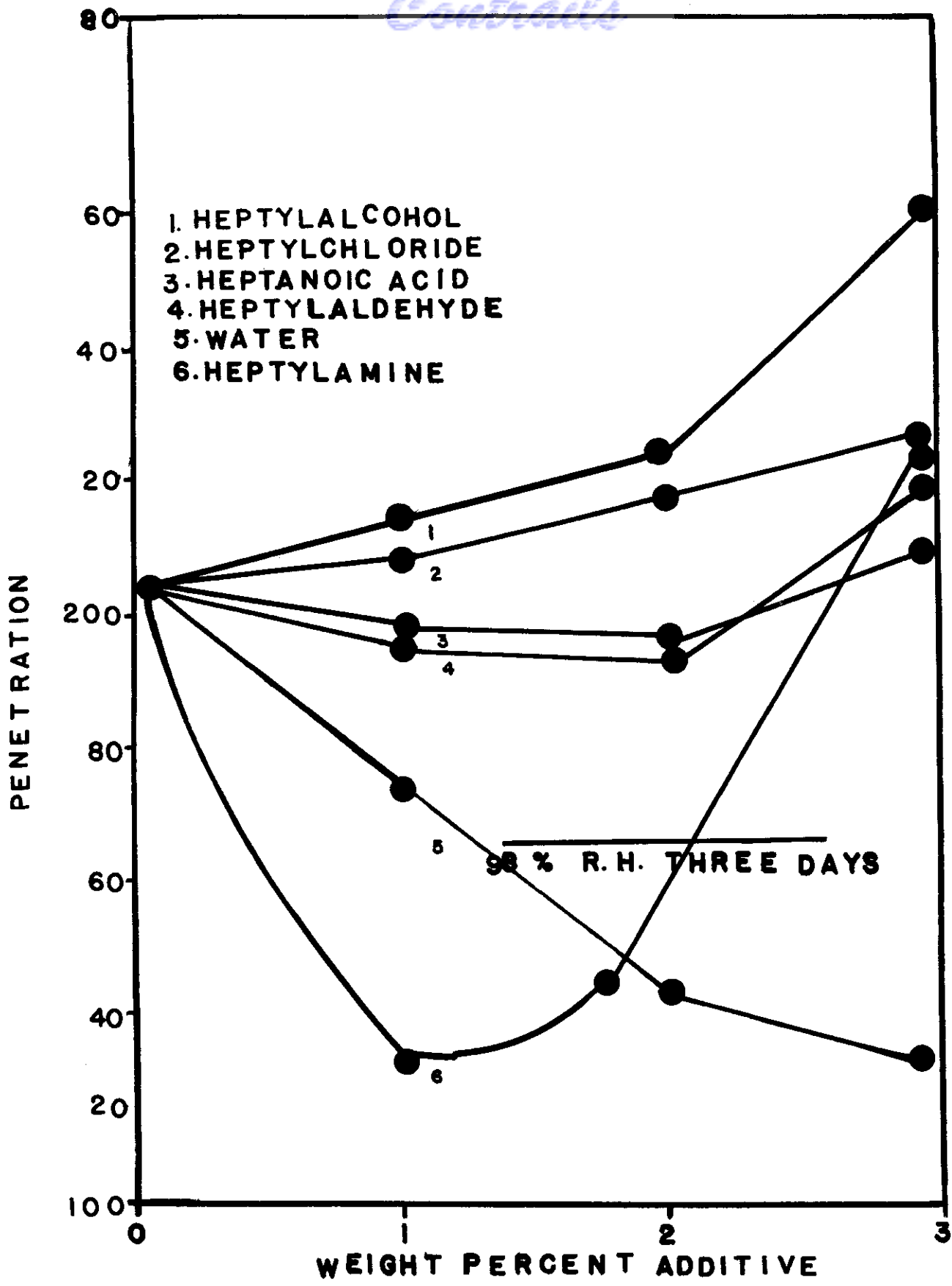


Figure 5. The Influence of Additives on an Aerosil-Plexol 201 Grease

Contrails

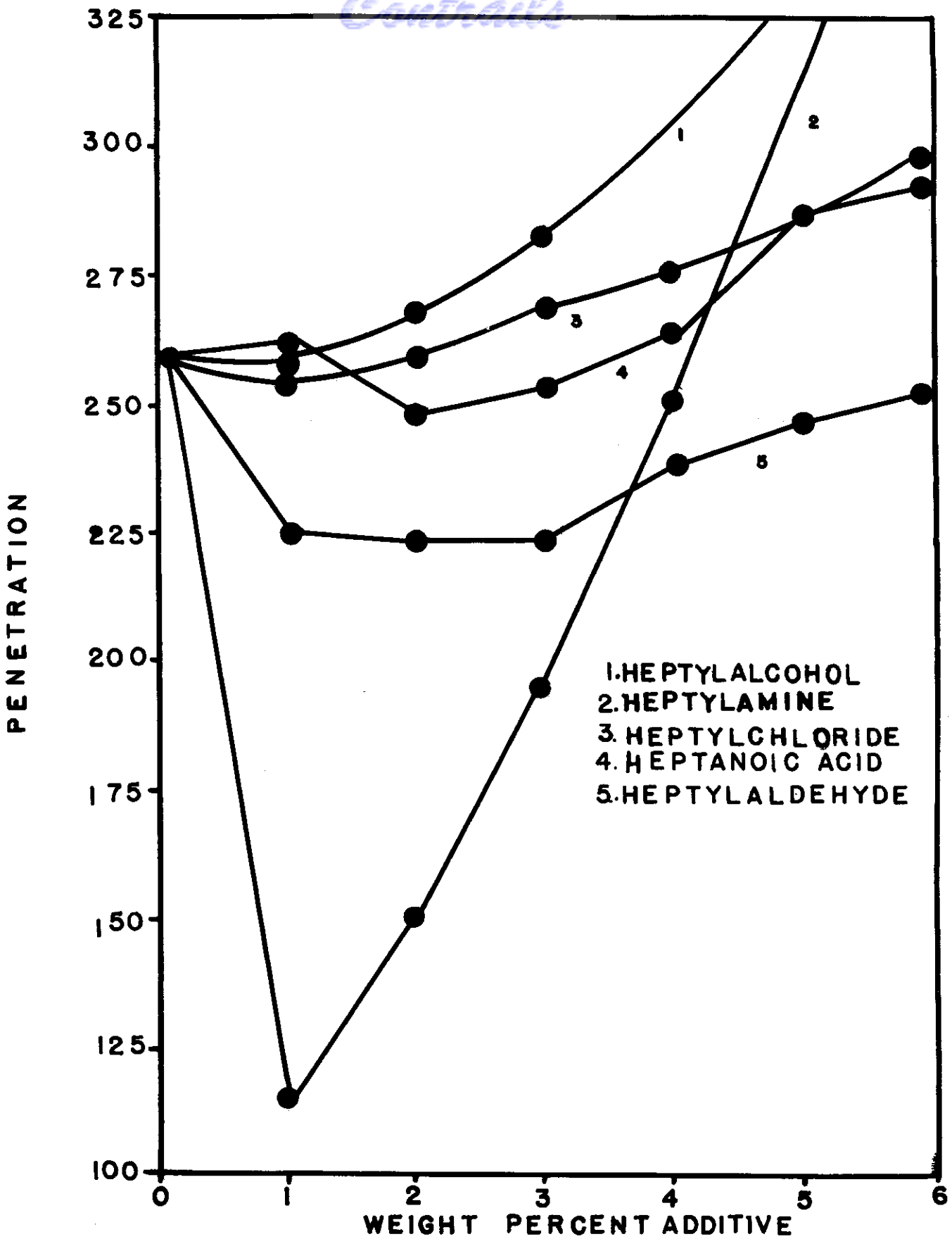


Figure 6. The Influence of Additives at High Concentrations on an Aerosil-Plexol 201 Grease

Contrails

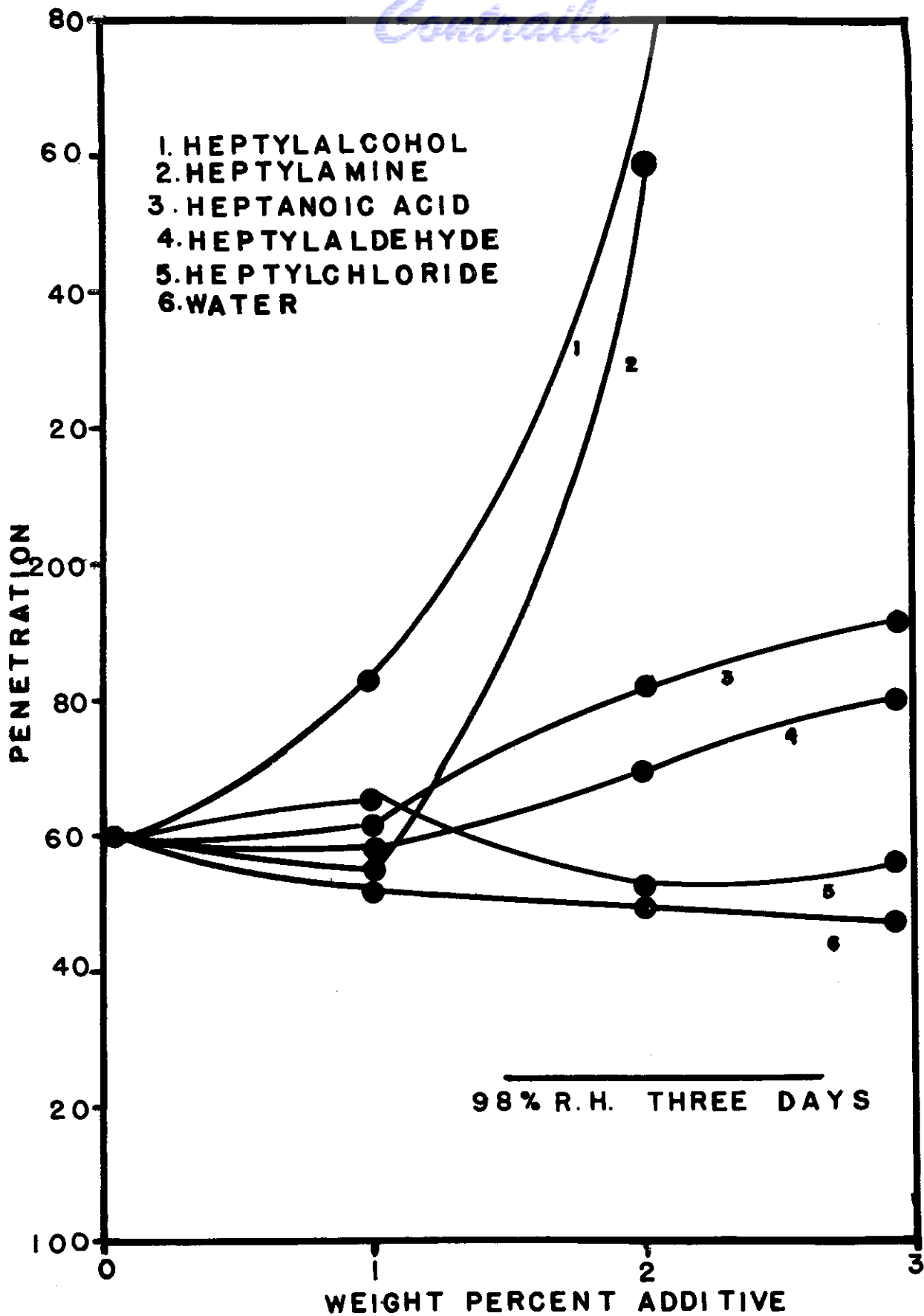


Figure 7. The Influence of Additives on a Hi Sil-Paraffin Oil Grease

Contrails

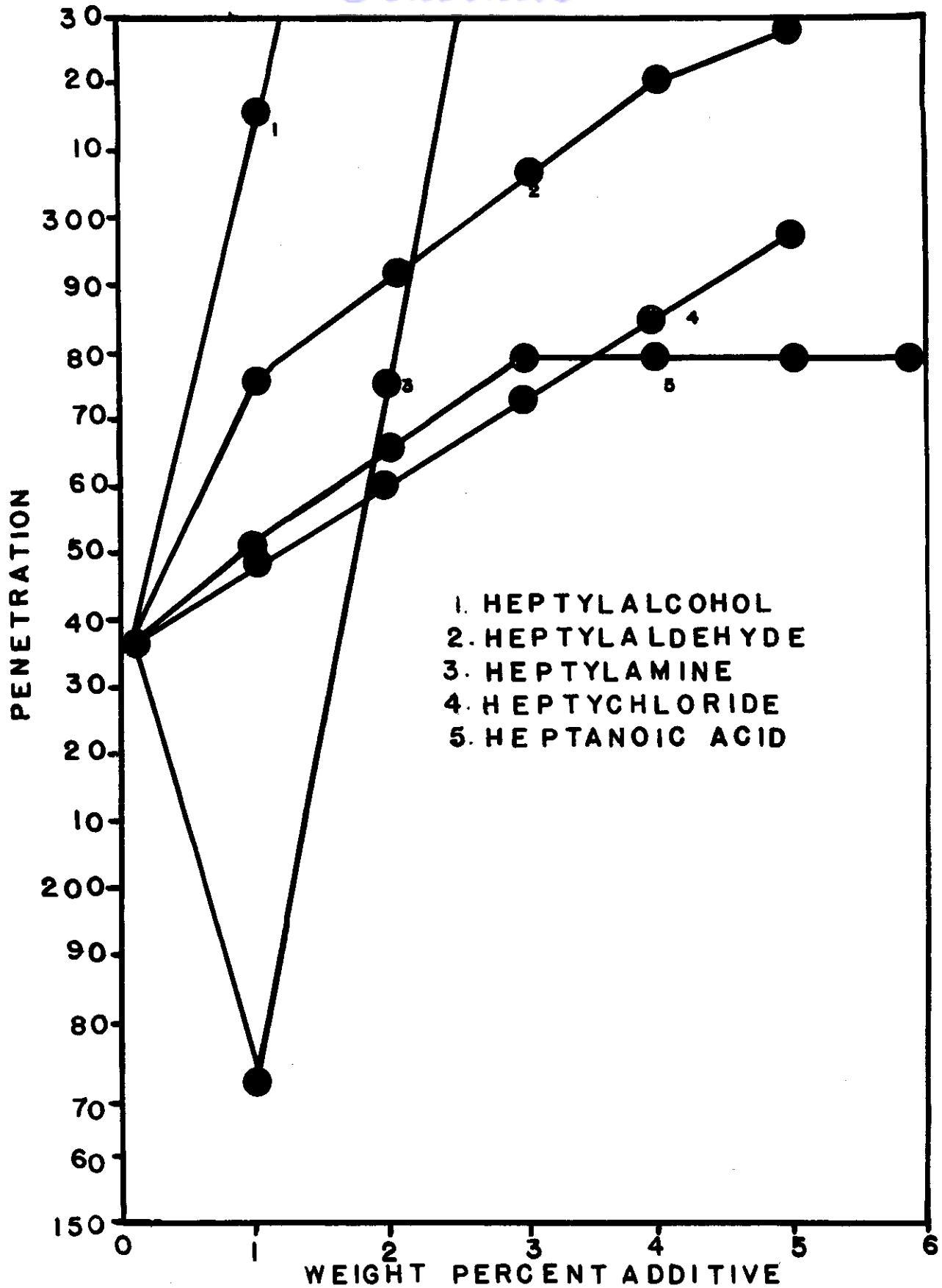


Figure 8. The Influence of Additives on a Hi Sil-Plexol 201 Grease

Further studies of the influence of additives on grease consistency were carried out with HiSil and two additional vehicles, Ucon Adipate and MLO-8220, and showed more strongly that the vehicle did not influence the relative additive behavior for a given solid. These results are illustrated in Figure 9.

Initial work with the more polar solid rutile in paraffin oil showed that not only did the alcohol and amine thin the grease at low additive concentrations but so also did the aldehyde. Recently it was found that all the heptyl additives used, except the chloride, thinned markedly; this behavior is illustrated in Figure 10. The chloride had no large effect on consistency but began to thin the grease at about 4 wt. %. It does appear, however, that additive influence with these polar solids is more pronounced as the polarity of the solid increases. For example, less alcohol is necessary to thin a rutile grease, than a HiSil grease and finally an Aerosil grease.

Grease Systems Containing Hydrophobic Thickeners - Another unexpected finding was the large influence of the heptyl additives on the system Estersil-paraffin oil. The nonpolar Estersil surface was not expected to have a large and specific adsorptive capacity for these additives yet marked differences in additive action was found experimentally. The influence of these same additives on the Estersil-paraffin oil system is markedly different from the Aerosil-paraffin oil system as shown in Figure 11. The changes in consistency of the Estersil greases are linear after a minimum of a certain amount of each additive is present, and the slopes of the curves at higher additive concentrations are nearly the same. The shapes of the curves can be explained by assuming the larger changes in consistencies at low concentrations are due to adsorption of the additive on the surface making the Estersil even more hydrophobic. After this initial large change, smaller and linear changes occur due to dilution of the grease by the liquid additives. This explanation requires that the surface has a different adsorptive capacity for each additive. Although this explanation is not completely satisfactory, there is no doubt that the Estersil surface contains polar sites which might be capable of adsorbing the additive molecules. These hydrophilic sites, as determined by water and nitrogen adsorption measurements, occupy the equivalent of 3.5% of the Estersil surface and are discussed fully in Section I.

Experimentally the carbon blacks were found to behave more like ideal hydrophobic solids when dispersed in grease vehicles. Greases prepared from Carbolac 2 in Sunvis 11 and Mogul in Plexol 201 did not undergo significant changes in consistencies with any of the heptyl additives or with water. Heat of wetting measurements, water adsorption studies and measurements of volatile matter content of

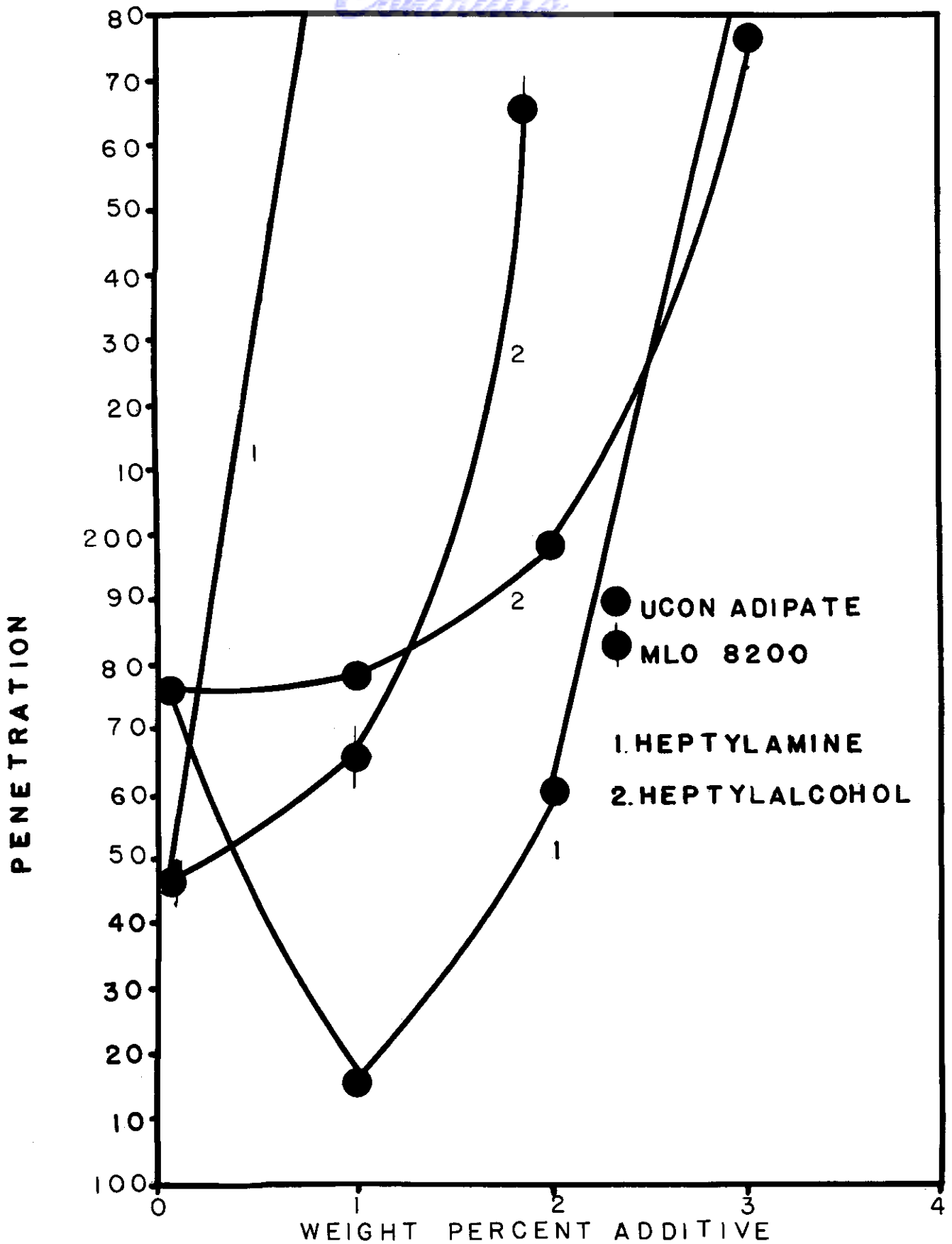


Figure 9. The Influence of Additives on Hi Sil-Ucon Adipate and Hi Sil-MLO8200 Grease Systems

Contrails

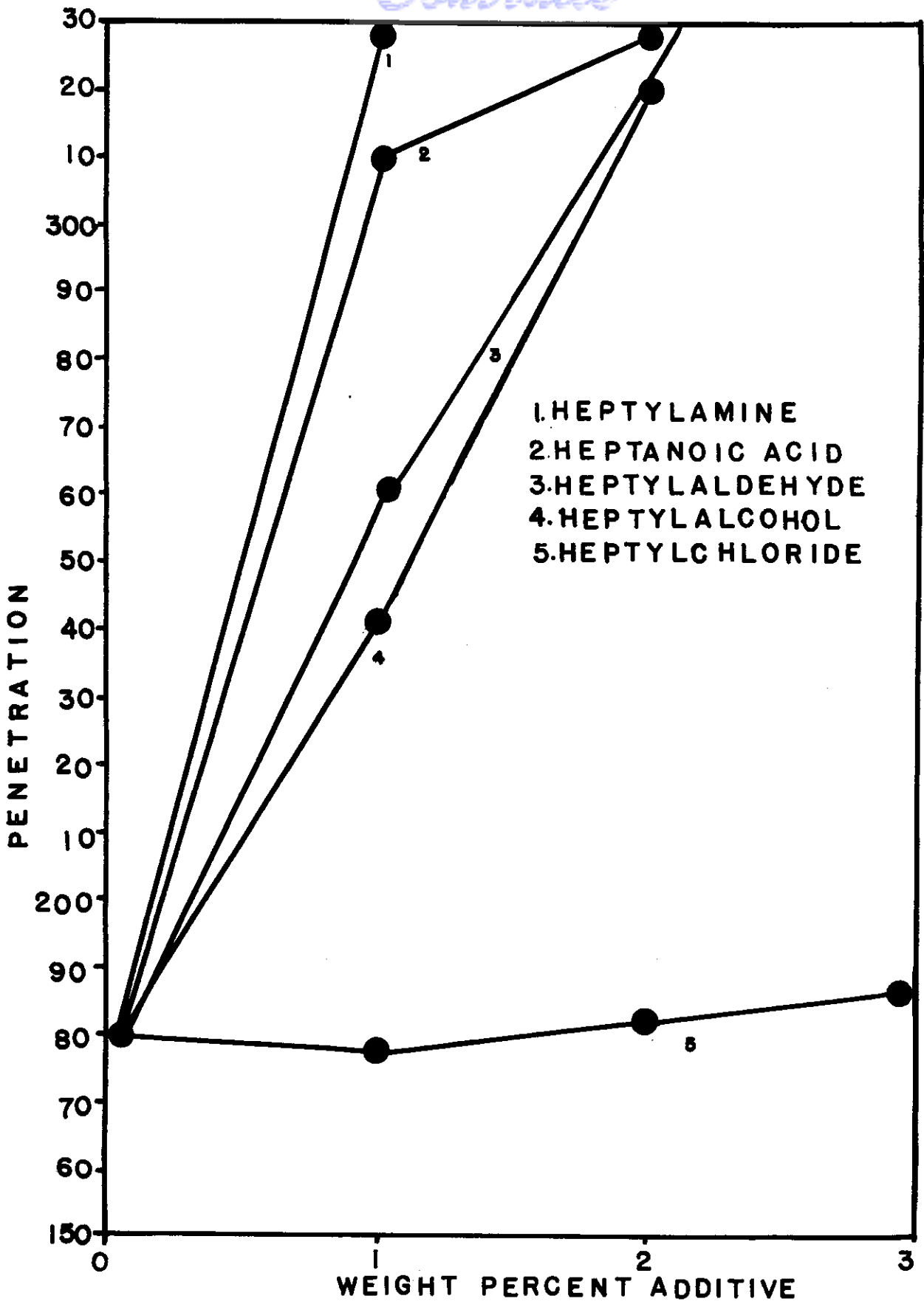


Figure 10. The Influence of Additives on a Rutile-Paraffin Oil Grease

Contrails

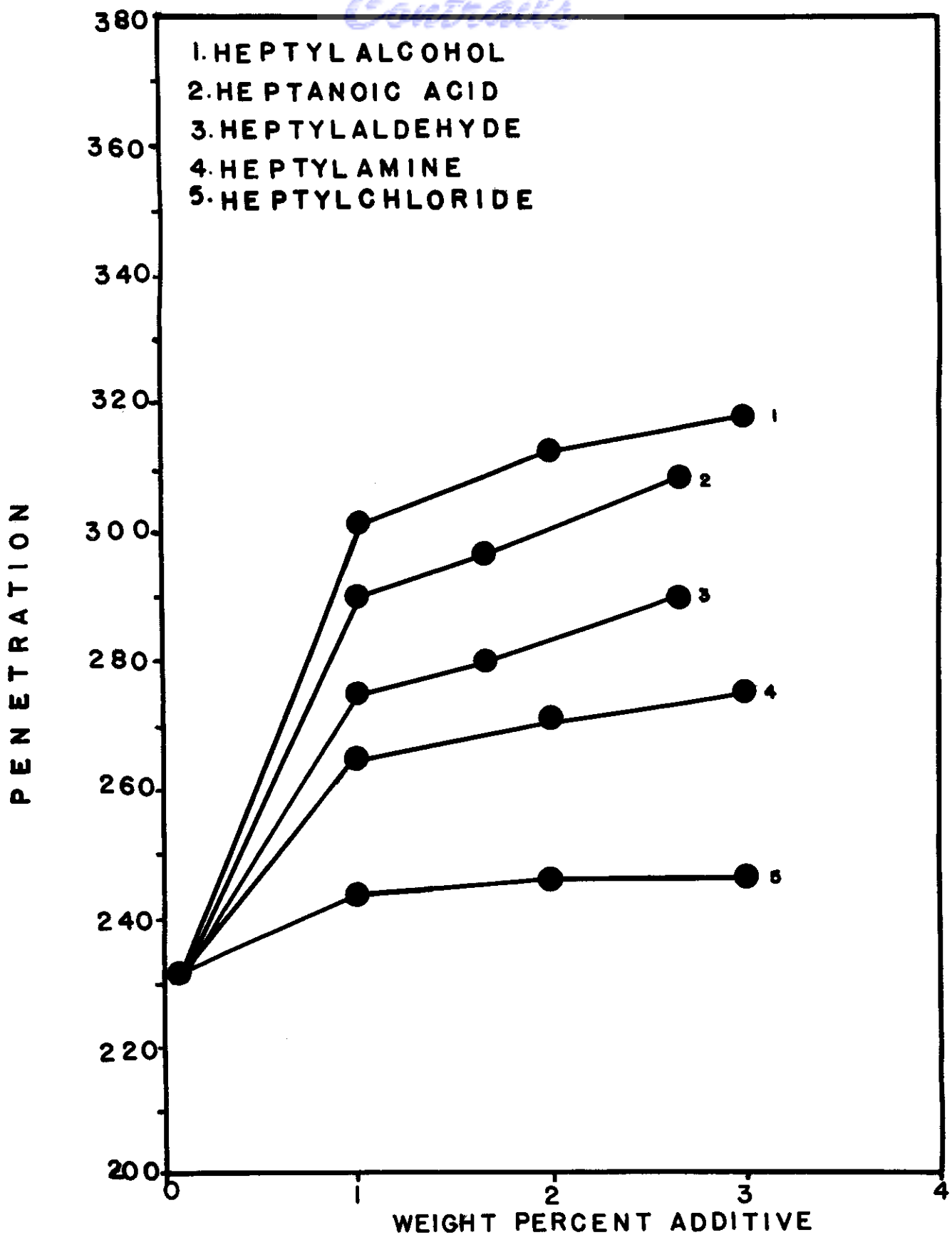


Figure 11. The Influence of Additives on an Estersil-Paraffin Oil Grease

Control

these solids all indicate the presence of polar, hydrophilic surface sites. Unlike Estersil, however, these sites are apparently unavailable for adsorption by additives in grease systems. The most likely explanation is that these polar sites are located in capillaries too small to admit the heptyl derivatives.

For the present, additive behavior can be summarized as follows:

1. The five heptyl derivative additives have the same relative effect on greases containing the silica, HiSil, dispersed in four different grease vehicles.

2. The additives have the same relative effect on HiSil and the less polar silica, Aerosil, also irrespective of the vehicle used.

3. The additive influence on the silica greases bear some resemblance to their influence on rutile built greases. The additives which most efficiently thin Rutile greases are also efficient in thinning silica greases. However, these additives, the acid and aldehyde, which have little effect on silica greases also markedly affect Rutile greases. Only the chloride has small effects on all systems. In effect, the grease containing the most polar solid is most influenced by additive action.

4. Estersil greases are also influenced by additives but not in a similar manner to the greases containing polar solids and they are deflocculated by a different mechanism.

5. The carbon black greases utilizing nonpolar grease vehicles are not significantly altered by the heptyl additives.

III. FUNDAMENTAL STUDIES OF NON-SOAP GREASE STRUCTURE

Electrokinetic Measurements of Non-Soap Greases.--Electrokinetic measurements were carried out to determine whether the dispersed phase in non-soap greases are electrically charged and whether electrostatic forces play a role in the formation of a grease structure. Two methods were used to study the electrical properties of grease systems. Microscopic investigations were made of greases under the influence of a variable electric field and conductance measurements were made for these same grease systems in another apparatus.

The behavior of the greases in an electric field was observed directly under the microscope. A special sample tube holder was made from an ordinary glass slide. Two strips of platinum foil were placed parallel to each other separated by a distance of 1 cm. and cemented to the glass. The grease sample to be tested was placed on the slide between the platinum strips. The slide was then placed under the microscope and the two platinum strips joined to a source of variable potential. The grease sample was observed carefully before any potential was applied and also as the voltage was applied and slowly increased from about 6 to 700 volts. The grease systems studied included Aerosil in Plexol 201, Estersil in Paraffin Oil, Bentone 34 in Plexol 201, copper phthalocyanine in MLO-8200. In no instance were any visible changes or movement of the thickener in the vehicle observed. It would appear from these studies that the solid particles in the non-soap grease systems studied are not electrically charged.

Conductance Measurements of Non-Soap Greases.--Preliminary measurements of the specific conductance of Aerosil-paraffin oil dispersions were made. A Wheatstone bridge circuit with a conductance cell as one leg of the bridge was used. The cell was composed of two platinum plates about 1 cm. square separated at a fixed distance of 2 mm. This cell was placed in the grease to be tested in such a way that the space between the plates was completely filled with grease. The cell was standardized with a solution of potassium chloride of known conductances. Conductance values are listed in Table X. Experimentally it was found that the conductance of the silica greases was of the order expected for the vehicle alone and did not show any marked change as the concentration of Aerosil was increased from 0.5 to 12.0%. Furthermore, no significant change in conductance was found when additives were used even though large consistency changes occurred. The results of these measurements apparently cannot be used to determine the structural arrangement of the thickener particles in the grease because of the low conductance of silica.

SPECIFIC CONDUCTANCE OF AEROSIL-PARAFFIN OIL GREASES

Wt. % Aerosil	Wt. % Heptyl Additive	Conductance ohms ⁻¹
0.5	----	7×10^{-11}
1.5	----	7×10^{-11}
2.5	----	7×10^{-11}
3.5	----	8×10^{-11}
4.5	----	8×10^{-11}
12.0	----	8×10^{-11}
12.0	3% n-heptyl alcohol	8×10^{-11}
12.0	3% n-heptyl aldehyde	8×10^{-11}
12.0	3% n-heptyl chloride	8×10^{-11}
12.0	3% n-heptanoic acid	8×10^{-11}

Grease structure studies were carried out on a carbon black-petroleum oil system (Carbolac 2-Sunvis 11) using conductance measurements. Regular and reproducible changes in conductivity were noted with increase in concentration of the black. The value for the specific conductance of a grease containing 12 wt. % solid was of the order of 10^{-5} ohms⁻¹. Because of the hydrophobic nature of the black, however, the heptyl additives decreased the consistency of samples of the 12 wt. % grease only slightly and small changes in resistances made exact measurements difficult. Nevertheless, conductance measurements support the view that these straight chain additives in general reduce gel structure and can be successfully used with carbon black greases. Additives which cause large changes in consistency, however, must be found for this purpose.

Exploratory Low-Angle X-Ray Studies.--Preliminary experimental X-ray measurements have been made on a few samples of Aerosil-thickened greases to evaluate low angle X-ray scattering as a method of studying structure. For this exploratory work the General Electric XRD-3 spectrogoniometer was used with the sample in the usual position for diffraction by the parafocusing "reflection" technique. The goniometer was aligned with care. Every adjustment was made to attain optimum resolution at a sacrifice of diffracted intensity. Grease samples were spread over the irradiated areas of 3-by 1-inch glass microscope slides and measurements of diffracted intensity made at angles between 0-to 1-degree 2-theta of arc. Chromium target X-radiation was used without a filter. No appreciable amount of K-beta radiation was observed.

Continued

The resulting patterns of diffracted intensity revealed the presence of appreciable maxima at surprisingly low angles in the samples possessing high consistency (as indicated by penetrometer readings in the neighborhood of 200). Those studied were: sample F-92, a dispersion of 10 percent G. S. hydrophobic silica in ethylene glycol; sample F-54, a dispersion of 12.2 percent Aerosil and 10 percent heptanoic acid in paraffin oil; and sample F-40, a dispersion of 15 percent Aerosil in Plexol 201. It appeared to make little difference whether hydrophilic or hydrophobic silica was employed as a thickener. Neither did the nature of the liquid vehicle appear to affect the results appreciably. On the other hand no X-ray peaks were observed with a copper phthalocyanine grease nor an Aerosil-thickened grease of low consistency. With various preparations of F-92, F-54, and F-40, scattering maxima were observed at diffraction angles corresponding to Bragg law spacings of approximately 1000, 650, 480, 300, 200, 130, and 95 Ångstrom units. With one sample a spacing of about 2000 Å was recorded. It appeared that the 2000, 1000, 650, and 480 Å peaks might be considered to be various orders of a significant long spacing in the grease structure.

In order to determine if the low angle patterns could be the result of factors other than the grease structures, some measurements were made with plain glass slides and with slides prepared by sprinkling dry Aerosil No. 2065 over a petroleum jelly-coated slide. The plain glass slide gave a peak at about 570 Å and the Aerosil-over-petroleum jelly slide a peak at about 460 Å with very weak peaks at 300 and 250 Å. The significance of the Aerosil-on-petroleum jelly results is not clear inasmuch as freshly-prepared slides with dry Aerosil surfaces gave no X-ray patterns. The peaks were recorded only after the Aerosil had settled in and been wet by the petroleum jelly.

Arrangements have been made to borrow two special slits from the General Electric Co. to define the X-ray beam on the XRD-3 instrument more precisely. These slits will give beam widths of 0.1 and 0.05 degrees. They will be accurately aligned in place and used to make transmission measurements of low-angle scattering. The X-ray beam will be passed directly through a thin, unsupported film of the grease sample and scattering data obtained on both sides of the direct beam. This technique should eliminate any artifacts inherent in the parafocusing reflection arrangement used for X-ray diffraction work on the spectrogoniometer.

Contrails
BIBLIOGRAPHY

1. Ryan, L. W., Harkins, W. D., and Gans, D. M., Ind. Eng. Chem. 24, 1288 (1932)
2. Galley, W., and Puddington, I. E., Can. J. Research, B21, 171 (1943)
3. Bloomquist, C. and Schutt, R., Ind. Eng. Chem., 32, 827 (1940)
4. Kruyt, H. R. and van Selms, F. G. Rec. trav. chim., 62, 407 (1943)
5. Young, G. J. WADC Technical Report 55-240, Basic Factors in the Formation and Stability of Non-Soap Lubricating Greases, April, 1955, from Surface Chemistry Laboratory, Lehigh University.
6. *ibid.*, p. 10.
7. J. W. McBain, "Colloid Science", D. C. Heath and Co., Boston, Mass., 1950, p. 46.

EVALUATION OF THE GARDNER MOBILOMETER FOR USE
IN MEASURING THE CONSISTENCY OF GREASES

In the past a Huber-Voet parallel plate viscometer was evaluated to determine whether it was suitable to measure the consistency of a grease. Although the instrument is cheap, easy to operate and gives fair reproducibility, it was concluded that for gels of the consistency encountered in this study the penetrometer is superior. As part of this program of instrument evaluation, a Gardner Mobilometer was examined and compared to the penetrometer in an attempt to find an instrument which would give a more meaningful index of grease consistency. The mobilometer consists essentially of a perforated piston contained in a close fitting cylinder. The piston is forced through the grease under constant load and the time for the piston to travel a definite distance is recorded.

Mobilometer data for a typical grease system are given in Figure 12 where the time for the piston to travel 10 centimeters is plotted as a function of the load on the piston. There is a minimum load below which no appreciable movement of the piston occurs. At loadings slightly higher than the minimum value, the rate of movement of the piston changes rapidly with load. At higher loadings a point is reached where the movement of the piston is nearly linear with the load and remains so down to times under one minute. Unfortunately, the experimental curves illustrated in Figure 12 were not easily reproduced for the thixotropic greases used. A wide range of values could be obtained depending on how long the grease was allowed to "Set-up" in the Mobilometer before readings were taken.

The time-load data could be plotted on a rate of shear-shear stress graph; however, because of the geometry of the system the calculation of an absolute rate of shear is difficult. The Mobilometer can not be used as a fundamental rheological instrument. With motor driven Mobilometers the piston is moved through the grease at a constant rate and the force is measured. This instrument also can not be used to obtain fundamental data of the flow properties of non-soap grease systems.

The minimum load at which noticeable movement of the piston can be observed is compared to the ASTM penetration values for a few grease systems. In Figure 13, the minimum load values are plotted against penetrometer readings. The linear relationship between the

Controls

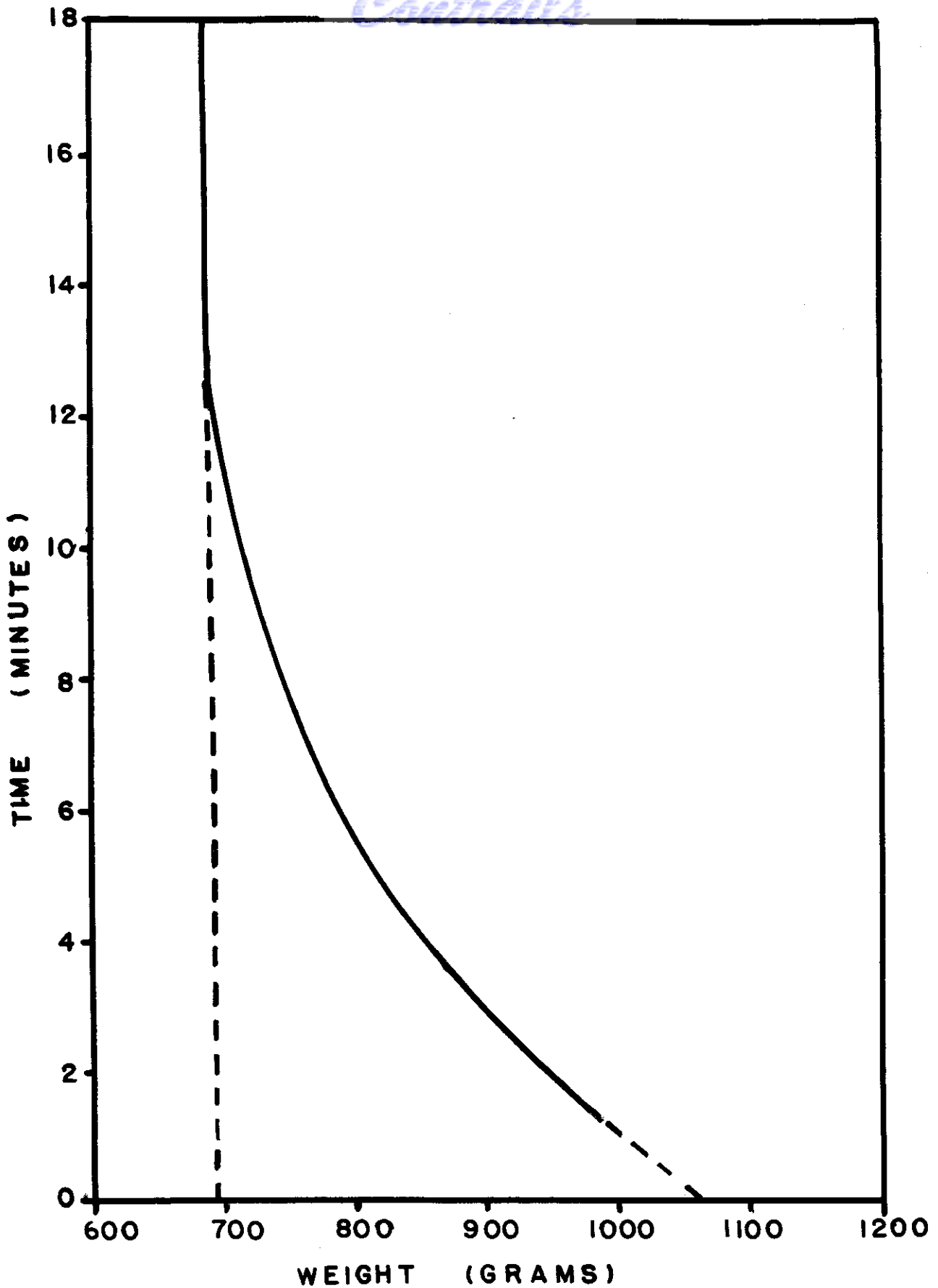


Figure 12. Typical Mobilometer Data

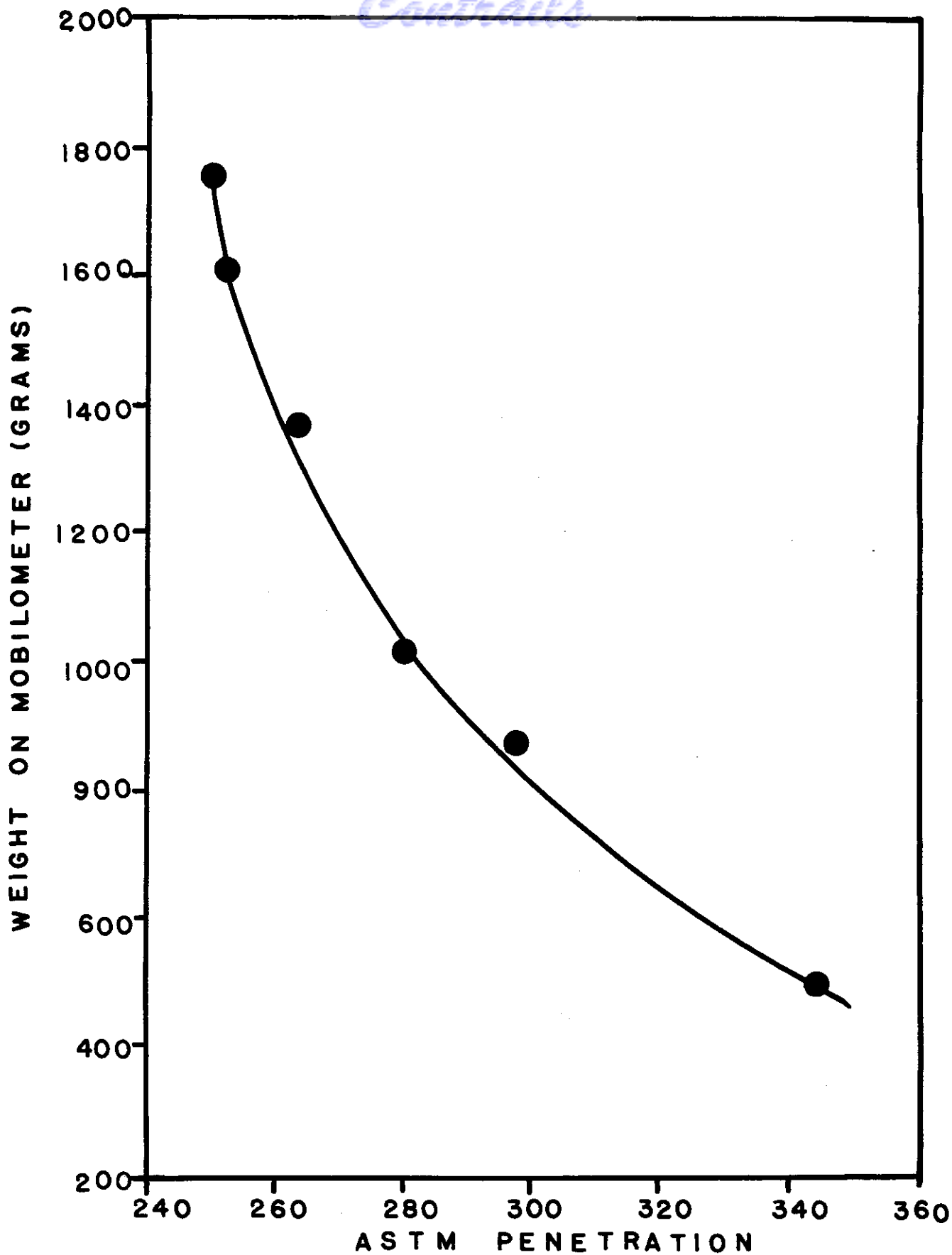


Figure 13. Comparison of Mobilometer and Penetrometer Data

Continued

results obtained with the parallel plate viscometer and the penetrometer indicated that the same property of the grease was measured in each case. Penetration appears to be a reciprocal function of the yield value of the grease. No such linear relationship exists between the Mobilometer and penetrometer data. Furthermore, although the curve of Figure 13 appears smooth, no great reliance can be placed on the minimum load values because of the difficulty in reproducing them.

On the basis of these studies it is concluded that the Mobilometer is not a satisfactory instrument for rheological studies of grease systems because:

1. There is poor reproducibility for thixotropic systems with slow build-up times.
2. It is very difficult to remove entrapped air when the grease is packed in the cylinder.
3. An absolute rate of shear cannot be readily calculated,

Surface Characteristics of Thickening Agents

Agent	Surface Area (m./g.)	Heat of Immersion in Water (ergs/cm ²)	Heat of Immersion in Plexol (ergs/cm ²)
Aerosil I	147	154	---
II	187	167	---
Santocel ARD	170	340	270
Permagel	~ 200	~ 500	180
Carbolac "1"	820-1000	80-90	115
Carbolac "2"	660-700	90	130
Carbolac "16"	525-600	110	---
Supercarbovar	350-430	85	120
Monarch "71"	250-420	65	110
G.S. Hydrophobic Silica Gel	270	26	85
Estersil	290-300	~ 10	66
Copper Phthalocyanine	74	34	112
Bentone "34"	6-11	440	250
Graphon	75-95	32	110
HiSil	129	460	---
TiO ₂ (MP997)	105	---	---
Fiber Glass	~ 3.0	---	---

Physical Properties of Oils

Oil	Density at 25° (g./ml)	Viscosity at 25° (Centipoises)	Surface Tension at 25° (ergs/cm ²)	Dielectric Constant at 25°
Plexol 201	0.912	17.6	31.3	3.85
Ucon Adipate 465	0.946	6.1	30.7	5.31
Paraffin Oil	0.873	87.5	31.0	--
Ucon Lubricant				
DLB-62-E	0.950	16.5	28.9	12.4
Sunvis 11	0.855	31.0	30.1	--
Circo X Light	0.910	38.6	31.6	--
MLO 8200	0.923	40.0	26.1	2.64
DC 550	1.062	129	27.1	--

RECEIVED
NOV 23 1956