Adsorption of Lubricating Oil Additives on Solid Surfaces (Part 2)[†]

Adsorption Behavior of Additives on Metal Surfaces by Ellipsometry

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Studies on the adsorption of lubricating oil additives are usually performed with powders although the lubricated surfaces are flat. In this study, the adsorption of such additives are determined on flat metal surfaces with an ellipsometer. The amount of adsorption has been found to be dependent on the cleanliness of the surface. The fast adsorption of BaDNNS was observed at the interface between gold/*n*-hexane. The type of adsorption curve is Langmuirian. The adsorbed film thicknesses of BaDNNS on gold, chromium, copper, stainless steel, and iron alloy range from 8 Å to 11 Å. The adsorbed film thicknesses of several additives range from 7 Å to 25 Å at gold/*n*-hexane interface. In two cases, the adsorption of lubricating oil additives was confirmed with Auger electron spectroscopy.

1. Introduction

Most of the lubricating oil additives are oil soluble surfactants and their actions are mainly based on adsorption on surface. Since lubricating oils are used in many machinery systems, it is important to know the adsorption behavior of the additives to understand their actions.

Studies on the adsorption of lubricating oil additives are usually performed with powders although the lubricated surfaces are flat. In this study, the adsorption of such additives are determined on flat metal surfaces by ellipsometry, a kind of spectrometry, which gives the film thickness of adsorbed layer by analyzing the state of polarization of the reflected light. The present study deals with the adsorption of the salts of dinonylnaphthalene-sulfonic acid (DNNS), ZnDiDP, and of other additives at interface between metal and *n*-hexane where gold surface was mainly used.

2. Experimental Section

2.1 Ellipsometry

In ellipsometry^{1),2)}, when elliptically polarized

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light shines onto a reflective surface, the reflected light changes its state of polarization in accordance with the surface condition. The ellipsometric readings give the phase shift and the azimuth angle. For a clean surface these give the optical constant of surface such as refractive index, and when the surface is covered with an adsorbed film these give the film thickness.

The ellipsometer used was Rudolph and Sons Inc. model 436/200E Type. Its components are arranged in **Fig. 1**. The light source is the 5,461 Å line from mercury lamp. The polarizer and the analyzer are mounted to give a circular scale of 360° and are read to 0.01 degree by vernier. The sample cell, made of aluminium block, is shown in **Fig. 2**. The port of the cell allows entrance and exit of light beam: 70° angle of incidence to specimen. The temperature of the solution, which was stirred with a polyethylene stirrer with magnet at the top end was controlled at 25±0.1°C.

2.2 Materials

Several kinds of metal surfaces were used as specimens. Chromium specimen was obtained by vapor deposition of chromium on flat glass for optical microscope use. Gold surface was obtained by vapor deposition of gold on the chromium specimen. The reason for gold deposition on chromium is to avoid easy breakage of gold film on glass. The copper specimen was a copper plate from Nippon Mining Co., Ltd. and the stainless steel plate was SUS 304 from U. S. Steel Corp. The iron alloy specimen was that for diesel engine cylinder liner material called Tarkalloy.

The gold and chromium specimens were cleaned

Table 1 Analysis of Surfactants

	Calculated		Found		Mwt	Specific Gravity
BaDNNS	Ba	13.00%	Ba	12.9%	1,057 ¹⁾	1.200
	C	63.65%	C	60.6%		
	H	8.20%	H	8.5%		
	Sulfated ash	22.09%	Sulfated ash	21.9%		
CaDNNS	Ca	4.18%	Ca	4.1%	959 ¹⁾	1.089
	C	70.10%	C	66.9%		
	H	9.03%	H	9.2%		
	Sulfated ash	14.19%	Sulfated ash	13.9%		
ZnDiDP	Zn	11.93%	Zn	11.8%	548 ¹⁾	1.227
	C	35.07%	C	35.3%		
	H	6.62%	H	6.9%		
	S	23.4 %	S	23.0%		
PDMA	C	74.3 %	C	74.1%	170,000 ²⁾	0.966
	H	11.5 %	H	12.1%		
	O	14.2 %	O	14.2%		

1) Calculated from structure
2) Information from manufacturer

Fig. 1 Ellipsometer Equipment

Fig. 2 Adsorption Cell

before adsorption experiment by treating with acetone, chromic acid-sulfuric acid cleaning solution,¹²⁾ and two times distilled water followed by drying under vacuum. Other metal surfaces were polished by fine particles of alumina with ethanol and washed with acetone. These surfaces were all mirror to the eye and flat.

The surfactants used were Ba-dinonyl-naphthalene-sulfonate (BaDNNS), CaDNNS, Zn-diisobutyl-dithio-phosphate(ZnDiDP), polydecylmethacrylate (PDMA), and other commercial additives such as ashless dispersants, detergents. BaDNNS and

CaDNNS, model compounds of detergent and rust inhibitor, are the same as those mentioned in a previous paper.³⁾ ZnDiDP is a typical antioxidant and antiwear agent, and PDMA is a model compound of polymethacrylate type viscosity index improver. These additives were synthesized by courtesy of the additive makers. Further purification was made by gum-membrance(dialysis) and chromatography. The typical analytical data of these surfactants are shown in **Table 1** and they agreed with the calculated data within the allowable limits of deviation. The *n*-hexane used was of analytical grade. It was treated with conc. sulfuric acid, sodium hydroxide followed by chromatography with silica gel and alumina; finally fractionally distilled, and the fraction with range of 68—69°C was recovered. Thus obtained *n*-hexane was further treated with metal sodium prior to adsorption experiment.

2.3 Experimental Procedure

After being cleaned, the surface specimen was attached to the holder in the cell in **Fig. 2**. *n*-Hexane was put into the cell and the whole cell was thermostatted at 25°C. Then a conc. surfactant solution was put into it with stirring. The solution was previously prepared by dissolving a

Table 2 Film Thickness of Stearic Acid Layer
(Å)

	Results in this Study by Ellipsometry	References
Monolayer	25.5 (on gold)	25 (on glass) by Ellipsometry ⁴⁾ 25 by Electron microscope ⁶⁾ 22.5 (on copper) by Ellipsometry ¹⁾
Triple layer	73 (on gold)

Fig. 3 A Model of Reflection on Adsorbed Film

surfactant into *n*-hexane so that easy mixing of the surfactant can be made in the cell. After attaining the adsorption equilibrium, the solution was removed from the cell; at the same time, the surface was rinsed with hexane, then dried.

The ellipsometric readings were made during these procedures. The phase shift Δ and the azimuth angle ψ were obtained.

2.4 Calibration of Film Thickness

Since the film thickness is given by computation in ellipsometry, it is necessary to calibrate it with actual data. Here, stearic acid was used for calibration.

The Langmuir-Blodgett method was applied to make a stearic acid film on gold surface. Monolayer and triple layer were checked. As seen from **Table 2**, the film thickness by ellipsometry in this study agreed with that of literature data^{1),4),6)} within the allowable limits of deviation. The computation of film thickness was made by the method described in the next section.

3. Computational Method for Film Thickness

The film thickness of the adsorbed layer is obtained from $\delta\Delta$ and $\delta\psi$ by making the measurements of Δ and ψ for clean surface and adsorbed surface. In other words,

$$\delta\Delta = \Delta - \bar{\Delta} \quad (1)$$

$$\delta\psi = \psi - \bar{\psi} \quad (2)$$

where, $\bar{\Delta}$ and $\bar{\psi}$ refer to the phase shift and azimuth angle for clean surface, while Δ and ψ are those for film covered surface.

Since the film thickness d is related to $\delta\Delta$ and $\delta\psi$, the major concern is to get the $d \sim \delta\Delta \sim \delta\psi$ relationship as a table or a graph. It is known

d is proportional to $\delta\Delta$ and $\delta\psi$ as long as the film thickness is thin.

McCrackin²⁾ and co-worker, and Archer⁵⁾ developed the computational methods for obtaining film thicknesses. The calculations are too complex because of use of complex functions. The method developed by McCrackin was used, and it is briefly described here.

In ellipsometry, the following relationship is given in the reflection model of **Fig. 3**.

$$\tan \psi \exp(j\Delta) = R_p/R_s \quad (3)$$

R_p and R_s are total reflection coefficients for the *p* wave and the *s* wave. They are expressed as follows.

$$R_p = \frac{r_{12}^p + r_{23}^p \exp D}{1 + r_{12}^p r_{23}^p \exp D} \quad (4)$$

$$R_s = \frac{r_{12}^s + r_{23}^s \exp D}{1 + r_{12}^s r_{23}^s \exp D} \quad (5)$$

where

$$D = -4\pi j n_2 \cos \Phi_2 d / \lambda \quad (6)$$

r_{12}^p , r_{12}^s , r_{23}^p , and r_{23}^s are Fresnel coefficients⁷⁾ expressed in Eq. (7)—Eq. (10).

$$r_{12}^p = \frac{n_2 \cos \Phi_1 - n_1 \cos \Phi_2}{n_2 \cos \Phi_1 + n_1 \cos \Phi_2} \quad (7)$$

$$r_{12}^s = \frac{n_1 \cos \Phi_1 - n_2 \cos \Phi_2}{n_1 \cos \Phi_1 + n_2 \cos \Phi_2} \quad (8)$$

$$r_{23}^p = \frac{n_3 \cos \Phi_2 - n_2 \cos \Phi_3}{n_3 \cos \Phi_2 + n_2 \cos \Phi_3} \quad (9)$$

$$r_{23}^s = \frac{n_2 \cos \Phi_2 - n_3 \cos \Phi_3}{n_2 \cos \Phi_2 + n_3 \cos \Phi_3} \quad (10)$$

where λ is the wave length of polarized light, n_1 , n_2 , and n_3 are the refractive indices of medium (solution), adsorbed film, and substrate(surface), respectively. Φ_1 , Φ_2 , and Φ_3 are the angles of incidence and those of refracted light, respectively. From Eqs. (3)—(10), the $d \sim \delta\Delta \sim \delta\psi$ relationship is obtained. The computation is too complex because the refractive index of surface usually includes an imaginary part and is expressed by a complex function. The computer programs were developed by McCrackin²⁾ and Archer⁵⁾. In the present study, NBS 479 computer program⁸⁾ by McCrackin was used.

As regards the refractive indices, n_1 and n_2 were measured with a refractometer and n_2 was also confirmed by ellipsometer. The results are shown in **Table 3**. Since n_3 , the refractive index of metal, cannot be measured with an ordinary refractometer, this was obtained from $\bar{\Delta}$ and $\bar{\psi}$ by ellipsometry and computation. Based on these refractive indices, various $d \sim \delta\Delta \sim \delta\psi$ data were ob-

Fig. 4a The Plots of $d \sim \Delta \sim \psi$ Relationship for Gold, Chromium, and Iron Alloy Surfaces at $n_1=1.3745$ (n -Hexane), $n_2=1.54$ (DNNS), by Computer Calculation

Table 3 Refractive Indices of Surfactants at 25°C (refractive index $n=N-jK$)

Surfactants	N	K
CaDNNS	1.543	0.01
BaDNNS	1.541	0.01
ZnDiDP	1.537	0.00
PDMA	1.474	0.00
n -Hexane	1.3745	0.00

tained, for it was necessary to have individual $d \sim \delta \Delta \sim \delta \psi$ data for every set of n_1 , n_2 , and n_3 .

4. Results and Discussion

4.1 The Refractive Index of Metal Surface and $d \sim \delta \Delta \sim \delta \psi$

In this study, the refractive indices of metal surfaces were obtained by making measurements of clean surfaces.

The refractive index n_3 is expressed in the form of $n_3=N-jK$, where N is the real part and K is the imaginary part, respectively. The latter appears when the material is absorptive; usually metal surfaces have K . Table 4 shows the refractive indices of each specimen obtained for the present experiments. Several repeated experiments were made by using different lots of surfaces, and some deviations of n_3 were found present, however, it does not affect the deviation of $d \sim \delta \Delta \sim \delta \psi$ rela-

Fig. 4b The Plots of $d \sim \Delta \sim \psi$ Relationship for Nickel, Copper, and Stainless Steel (SUS 304) at $n_1=1.3745$ (n -Hexane), $n_2=1.54$ (DNNS) by Computer Calculation

Table 4 Refractive Indices of Metal Surfaces measured in n -Hexane at 25°C (refractive index $n=N-jK$)

Metal	N	K
Gold	0.4098	2.3112
Chromium	2.4759	2.6898
Copper	0.9658	2.3933
Stainless Steel*	2.4926	3.9413
Nickel	1.7579	2.9918
Iron Alloy	2.3888	3.2957

* SUS 304

tionship.

In Figs. 4a and 4b are shown the plots of $\Delta \psi$ for each metal surface with changing film thickness d in the typical case of refractive indices ($n_1=1.3745$, $n_2=1.54$). From the figures it is apparent that Δ and ψ make loops in the whole range of film thickness. Within a small range of film thickness, Δ decreases while ψ increases with increasing film thickness d , and the change of ψ is far smaller than that of Δ . Thus, $\delta \Delta$ was used exclusively in the present experiment except in exceptional cases.

Fig. 5 illustrates the relationship between film thickness d and $\delta \Delta$ in each metal surface for BaDNNS film. The slopes of the $d-\delta \Delta$ lines vary because of the differences in the metal refractive indices. It can be seen from the figure that d

Fig. 5 A Plot of Film Thickness d against $\Delta\delta$ for Metal Surfaces in n -Hexane at 25°C by Computer Calculation (BaDNNS)

Fig. 6 Adsorption of BaDNNS at Interface between Gold and n -Hexane at 25°C , BaDNNS Concentration 10^{-3} mol/l

is proportional to $\Delta\delta$ in such a small range of film thickness.

4.2 Adsorption of Lubricating Oil Additives

Fig. 6 shows the adsorption behavior of BaDNNS on gold surface from n -hexane solution. As seen from the curve(1) the adsorption rate of the sulfonate is fairly large. The same tendency was obtained also in the case of CaDNNS. Smith and coworker⁹⁾ reported that it took about 100 min. to attain equilibrium for adsorption of DNNS in white oil with stirring whereas it took 4,500 min. without stirring. These results suggest that adsorption rate depends on diffusion rate as F.M. Fowkes¹⁰⁾ pointed out. Since the diffusion coefficient includes viscosity of fluid, the flux is considered to be dependent on viscosity. In this study, n -hexane, which is a low viscosity solvent, was used. That may be the reason for the rapid ad-

Fig. 7 Adsorption of ZnDiDP at Interface between Gold and n -Hexane at 25°C , ZnDiDP Concentration 10^{-3} mol/l

sorption of DNNS observed.

In the present experiment, it was found that surface condition of the surface examined significantly affected the adsorption of surfactants. **Fig. 6** curve(2) shows that the adsorption film thickness is very small in the case of the nonactive surface that was obtained by immersing the gold surface in analytical grade n -hexane (no further purification was made) for more than 48 hrs, while the clean surface gives much greater adsorption film thickness.

The same phenomenon was observed in the case of ZnDiDP as shown in **Fig. 7** too. A possible reason for that can be considered as follows. The clean surface has high surface energy, hence any adsorption species in the medium (solvent) may be adsorbed on the surface to lower the surface energy regardless of the kind of adsorption species. If impurity is first adsorbed irreversibly on the same adsorption site as that of the additive, the succeeding adsorption of the additive may be weakened.

Fig. 8 shows the concentration dependence of BaDNNS adsorption on gold surface, and the adsorption curve is of Brunauer's TYPE I. **Fig. 9** shows a Langmuir plot for data in **Fig. 8**. A linearity was obtained.

As seen in **Fig. 8**, BaDNNS is adsorbed on the surface even at very low concentrations. It is obvious that concentration of 10^{-5} mol/l was sufficient to attain the saturation of adsorption to form a monolayer. Also it was found that adsorption of BaDNNS occurred even at 10^{-7} mol/l , which may be of the critical micelle concentration.

Table 5 shows the film thicknesses of BaDNNS obtained on various metals at 25°C , 10^{-3} mol/l in hexane. Based on the results, the film thickness of the adsorbed layer of BaDNNS is $8\sim 11 \text{ Å}$ regardless of the metals studied. Despite the film

Fig. 8 Adsorption Isotherm of BaDNNS at Interface between Gold and *n*-Hexane at 25°C

$C/\theta = C + 1/K$ was applied, C : Concentration of BaDNNS, θ : Surface coverage, K : Constant

Fig. 9 A Langmuir Plot for $C/\theta \sim C$ of BaDNNS Adsorption at Interface between Gold and *n*-Hexane at 25°C

thickness being almost the same, $\delta\Delta$ is different in each metal. This is caused by the differences in the refractive indices of metal surfaces. Since there was some deviation in the $\delta\Delta$ values for different lots of specimens used, repeated experiments were conducted. The data in **Table 5** show the average values of film thicknesses. In the case of gold surface, the mean value of $\delta\Delta$ is -0.274 ± 0.015 degree by statistic *t*-inspection of 95% reliability based on more than 20 experiments. That leads to a mean film thickness of BaDNNS $d = 9.9 \pm 0.5$ Å.

The film thickness of BaDNNS was also measured in the air medium, and $d = 11.6 \pm 1.8$ Å (95% reli-

ability by statistics) was obtained. The procedure was as follows: After attaining the adsorption equilibrium of BaDNNS on gold, the solution was removed and, at the same time, the surface was rinsed with *n*-hexane and dried. Ellipsometric readings were then made and d was calculated.

This result suggests that the adsorption of BaDNNS on gold from *n*-hexane is fairly strong because BaDNNS remained on the surface even after rinsing with *n*-hexane and no desorption was observed.

Table 6 shows the film thicknesses of other additives adsorbed also on gold surface from *n*-hexane solution. The concentration examined was 0.1 wt% for each, as this value of concentration was sufficient to form a monolayer based on preliminary experiment. As seen from the table, CaDNNS showed almost the same film thickness as BaDNNS. The area per molecule was 146 Å^2 for BaDNNS and 145 Å^2 for CaDNNS assuming that the adsorbed molecules formed a closely packed monolayer. Smith reported the occupied area of CaDNNS was 125 Å^2 from the force-area curve assuming also a closely packed layer.

With regard to the film thickness of sulfonate, there is almost no comparable study but there is a related work. According to Fowkes et al⁽¹⁾, the micelle size of CaDNNS in *n*-decane is about 47 Å by six molecules in the long diameter of a micelle and 24 Å in the short diameter, and one compartment of CaDNNS is 12 Å. Considering these data the adsorbed layer of both BaDNNS and CaDNNS in this study would be mono-and

Table 5 Film Thicknesses of BaDNNS on Various Metal Surfaces in *n*-Hexane at 25°C

Metal	Gold	Copper	Stainless Steel	Chromium	Iron Alloy
$\delta\Delta$ Degree	-0.27	-0.25	-0.58	-0.40	-0.48
Film Thickness Å	9.9	8.4	9.3	8.5	10.7

(The concentration of BaDNNS : 10^{-3} mol/l)

Table 6 Film Thicknesses of Adsorbed Layers of Lubricating Oil Additives at Interface between Gold and Hexane at 25°C
(concentration : 0.1 wt% in *n*-hexane)

No.	Additives	Type	Mwt	Film Thickness (Å)
1	CaDNNS	Ca-sulfonate	959	10
2	ZnDiDP	Zn-dialkyl-dithio-phosphate	548	7
3	PDMA	Polymethacrylate	~170,000	16~20
4	V. I. Improver-1	A derivative of polymethacrylate	~250,000	19~25
5	Dispersant-1	A derivative of succinimide	~ 2,200	18~23
6	Detergent-1	A synthetic Ca-sulfonate	~ 1,200	18
7	Detergent-2	A natural Ca-sulfonate	~ 1,200	17

Table 7 Comparison of Adsorbed Film Thicknesses in Different Systems

	Solvent	Surface	Film Thickness (Å)	Literature
PAN-PG ^{c)}	decaline dodecane	silica	larger than PLMA ^{a)}	14)
PLMA	same	silica	25±10	13)
PAM-VP	same	silica	210±40	13)
PDMA	<i>n</i> -hexane	gold	16~20	(this study)
Polystyrene	cyclohexane	chromium	400~500	12)

- a) Total surface coverage is 2.4—2.6 fold as large as PLMA
b) Estimated from carbon black sedimentation experiment
c) polyglycol methacrylate

closely packed layers.

A typical antioxidant and antiwear agent ZnDiDP showed a slightly smaller film thickness than DNNS. This may be caused by its smaller molecular weight and shorter alkyl chain.

Viscosity index improver, PDMA, and a commercial polymethacrylate type polymer(defined as V.I. improver-1) were examined. Their typical adsorption film thicknesses were 16—25 Å in the present experiment as shown in **Table 6**. Their film thicknesses are far smaller than those anticipated from their general molecular weights. This can be considered as follows. **Table 7** summarizes the film thicknesses of some polymers adsorbed on solids. In the case of polystyrene¹²⁾ on chromium from cyclohexane, the film thickness is 400—500 Å where a swollen model was proposed. Fontana et al. reported¹³⁾ on the adsorption of some derivatives of polymethacrylate(copolymer) on silica. They compared the adsorption behaviors of PLMA (polylaurylmethacrylate) and PAM-VP(copolymer of stearyl methacrylate and N-vinyl-1-2-pyrrolidone). They reported the film thickness of PAM-VP was 210±40 Å, while that of PLMA was 25±10 Å by sedimentation velocity method as shown in **Table 7**. From a further study¹⁴⁾ it is suggested that the difference was caused by the preferential adsorption of the repeating unit in the polymer structure and by orientation of the adsorbed polymer: Since PLMA is homopolymer, every segment tends to be equally adsorbed on the surface. This causes horizontal adsorption with thin film thick-

ness. On the other hand, PAM-VP have two different segments, one of them is preferentially adsorbed on the surface while the other is directed to bulk solution, giving a thicker film.

Since the present experiment was performed by using homopolymer at low concentrations, it was considered that the polymer was adsorbed on the surface in horizontal orientation with thin film thickness. At higher concentrations or in a different solvent, different configuration may be possible. A further study is needed for that.

In **Table 6** are reported also some results of other commercial additives such as ashless dispersants, detergents etc. They range also around 20 Å, which is greater than the film thickness of DNNS.

4.3 Surface Analysis by Auger Electron Spectroscopy

Auger analysis was made in order to confirm the adsorption of surfactants. The specimens for analysis were obtained as follows: After attaining adsorption equilibrium, the surface was rinsed with *n*-hexane and dried under vacuum, then it was examined for which a Scanning Auger Microprobe PHI 590 (Physical Electronics Industry Inc.) was used under the following conditions : of *E_p*=5 kV; beam diameter=5 μm at 5×10⁻⁹ Torr.

Fig. 10 shows two cases of adsorbed layer. In each case, the specific metal elements Ba or Ca was found in the spectra of BaDNNS and CaDNNS: the presence of these surfactants was recognized on the surface.

Fig. 10 Auger Spectra of Adsorbed Film of BaDNNS and CaDNNS on Gold

5. Conclusions

The adsorption of lubricating oil additives was studied by ellipsometry using flat reflective metal surfaces and the following results were obtained.

- (1) The adsorbed film thickness of lubricating oil additives can be obtained by ellipsometry in solution adsorption.
- (2) The amount of adsorption is dependent on cleanliness of the surface examined.
- (3) The adsorbed film thickness of BaDNNS is not influenced significantly by kinds of metals. It ranges from 8 to 11 Å on gold, chromium, copper, stainless steel, and iron alloy. The average film thickness on gold was around 10 Å at saturation of adsorption with the formation of a monolayer.
- (4) The adsorbed film thicknesses of several additives range from 7 to 25 Å. Among them polymethacrylate type viscosity index improvers exhibit thin film thicknesses inspite of their large molecular weights. This may be caused by horizontal ori-

entation.

(5) The adsorption of lubricating oil additives is also confirmed by Auger electron spectroscopic analysis.

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要 旨

潤滑油添加剤の固体表面への吸着（第2報）金属表面における
吸着挙動のエリプソメトリー法による検討田村 邦光^{*1)}, James T. Tse^{*2)}, Arthur W. Adamson^{*3)}

潤滑油添加剤の作用は金属表面への吸着現象に基づくことが多い。従来、潤滑油添加剤の吸着研究は粉体を用いて行われることが多いが、現実の系では金属面が対象となる。そこで本研究ではエリプソメトリー法を適用し金属平面への添加剤の吸着挙動を検討した。特に、これまで添加剤の吸着膜厚さについての研究例は少ないのでこれを中心に検討を行った。

その結果、以下の事柄がわかった。エリプソメトリー法はだ円偏光を反射表面にあて、吸着膜による光の位相変化をとらえて膜厚さを測定する方法であるが、吸着膜厚さ d は位相変化 δA と関連付けられ、膜厚さが小さい範囲では Fig. 5 のように d は δA に比例する。この直線のこう配は金属表面の屈折率により異なる。Table 4 にエリプソメトリー金属表面の屈折率を示した。

金/ n -ヘキサン界面における BaDNNS の吸着は Fig. 6 からわかるように速やかに行われ、短時間で平衡に達する。これはヘキサンが低粘度であり BaDNNS の拡散が速やかに行われ

るためと思われる。また吸着は表面の清浄度に極めて敏感に影響をうけ、Figs. 6 および 7 の曲線 (2) にみられるように若干でも汚損されると添加剤の吸着量は減る。

Fig. 8 は BaDNNS の金/ n -ヘキサン界面における吸着の濃度依存性を示すが、低濃度から立ち上がり一定値に達する。これは Brunauer の TYPE I の等温線に相当する。このラングミュアプロットは Fig. 9 のように直線を示すことから、BaDNNS は金表面に単分子吸着をしているものと考えられる。

Table 5 は各種金属（金、クローム、銅、ステンレス、鋳鉄）に対する BaDNNS の吸着膜厚さを示すが、金属間で大差はなく 8~11Å と推定された。

Table 6 はその他の潤滑油添加剤についての吸着膜厚さを示す。CaDNNS は BaDNNS と同程度の膜厚さを示し、1分子当たりの占有面積はいずれも 140~150Å² と推定された。また ZnDiDP については DNNS 塩より少ない膜厚さを示した。

他方、粘度指数向上剤については 16~25Å と分子量のわりには小さい膜厚さを与えたが、これは表面で吸着分子が水平配向をとっていることによるものと考えられる。

また、金表面で吸着が行われていることは Fig. 10 に示すようにオージェ電子分光法により確認された。

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