

JOURNAL OF THE OIL AND COLOUR CHEMISTS' ASSOCIATION



Vol. 50 No. 9

September 1967

INTERFACIAL BEHAVIOUR

Dispersion

The adsorption of long chain acids on to rutile
from n-heptane

Adsorption of polyamides. Infra-red measurements of
the interaction with rutile and carbon black surfaces

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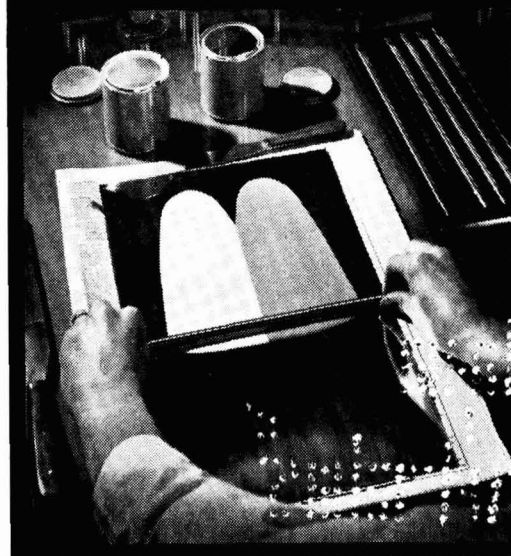
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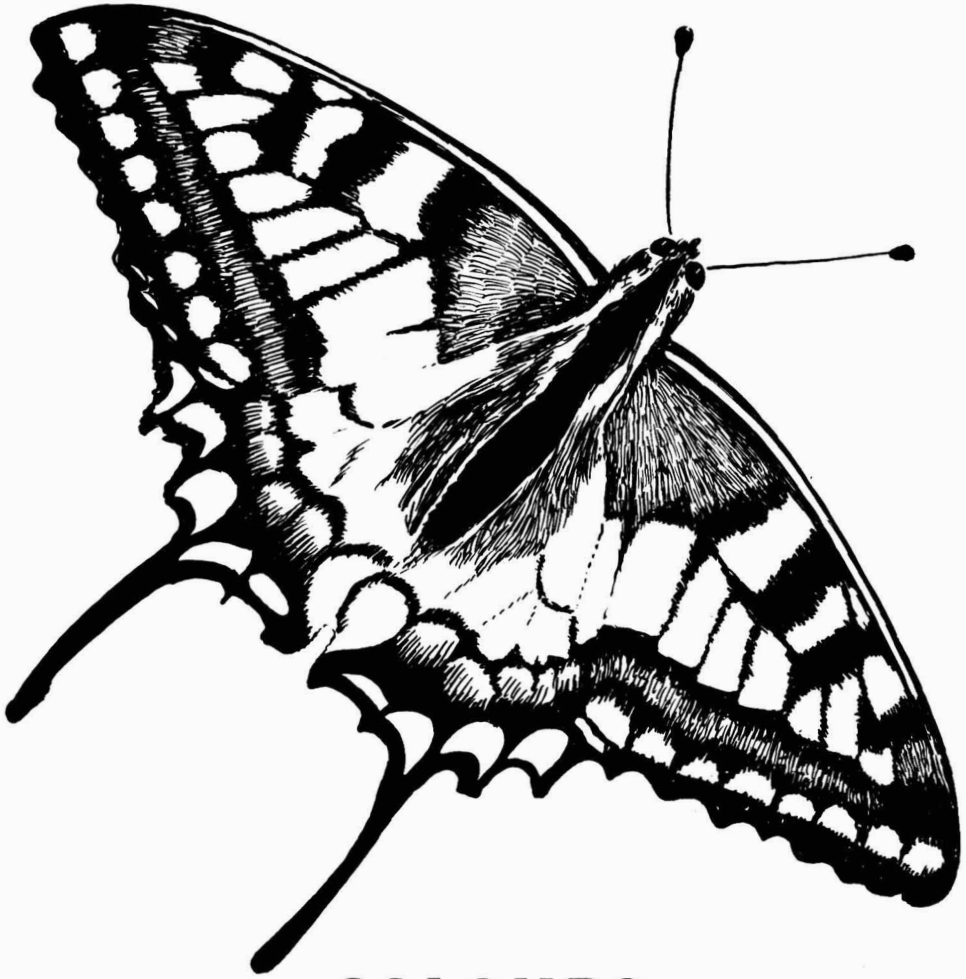
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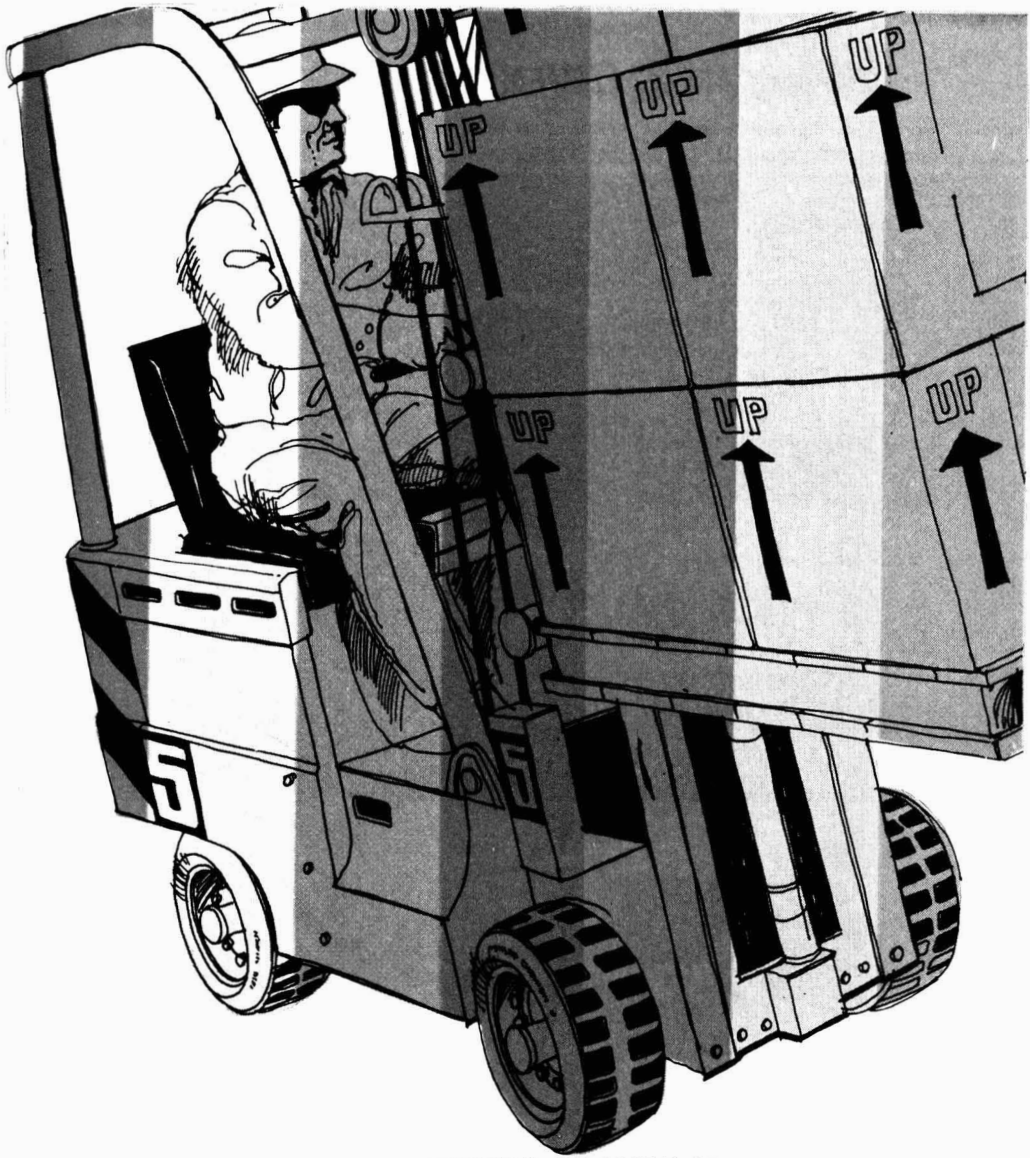
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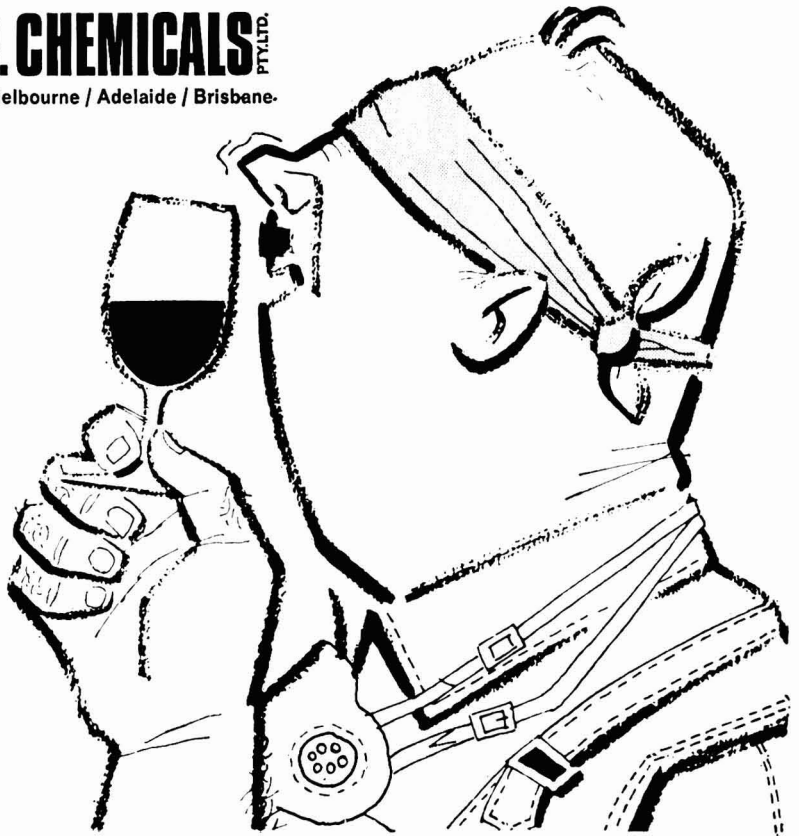
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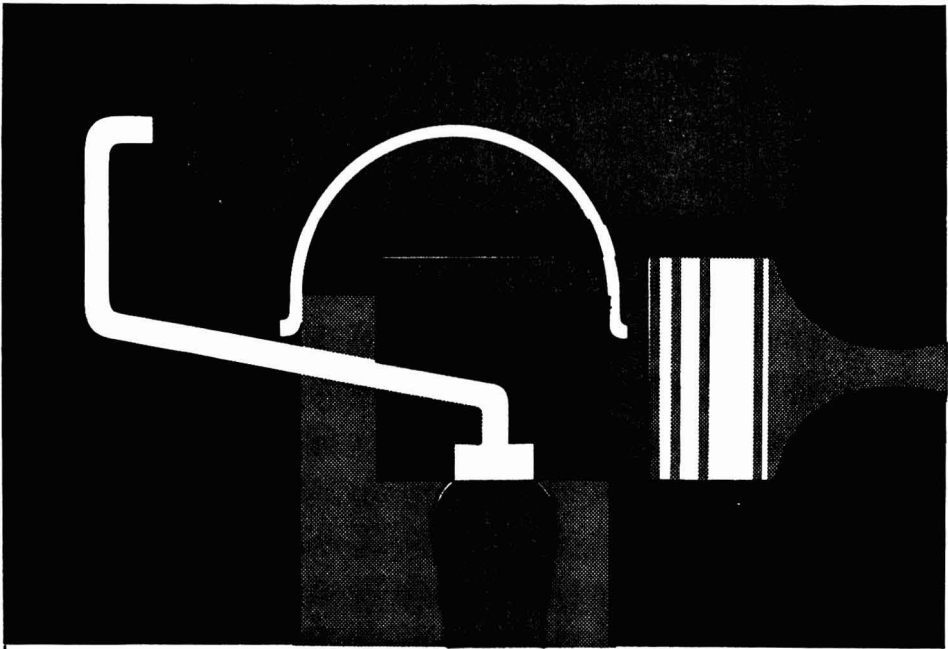
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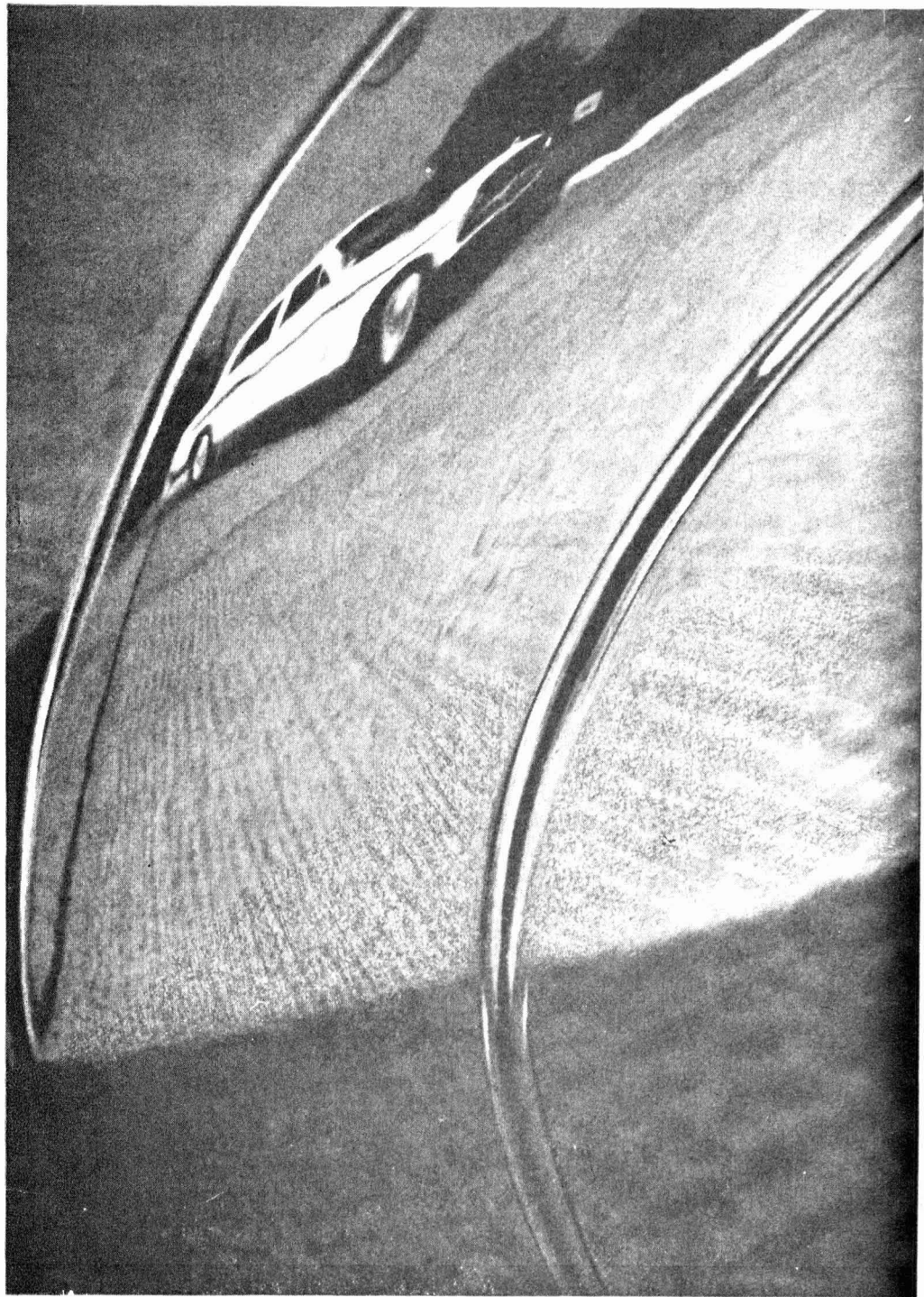
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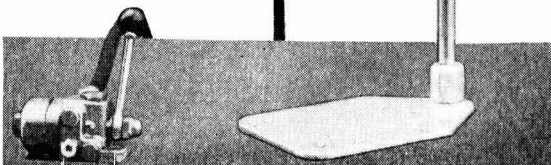
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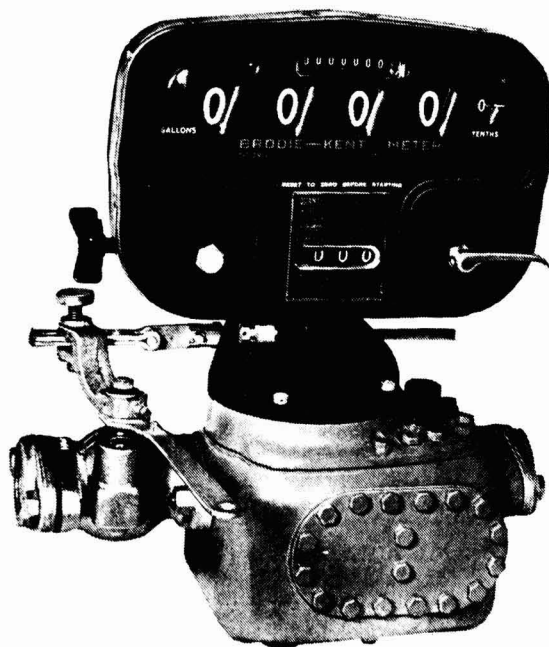
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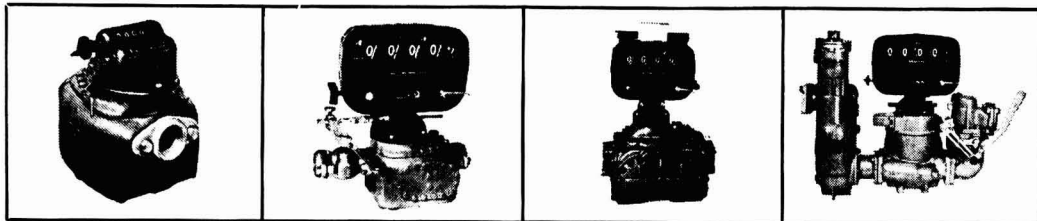
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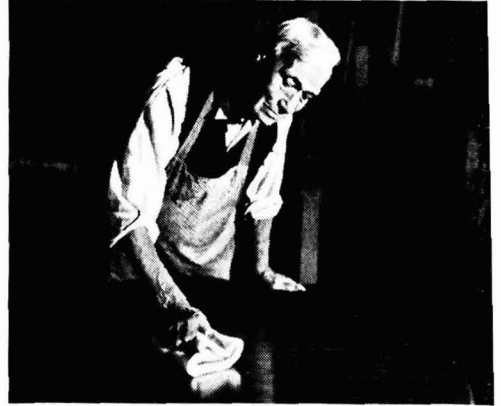
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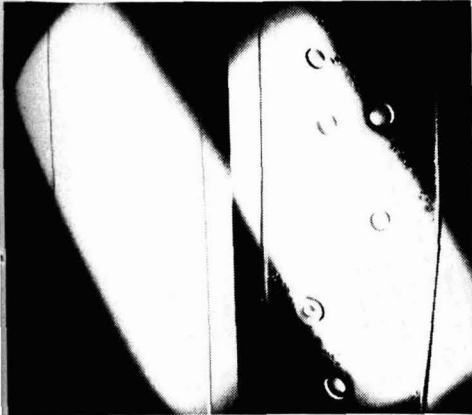
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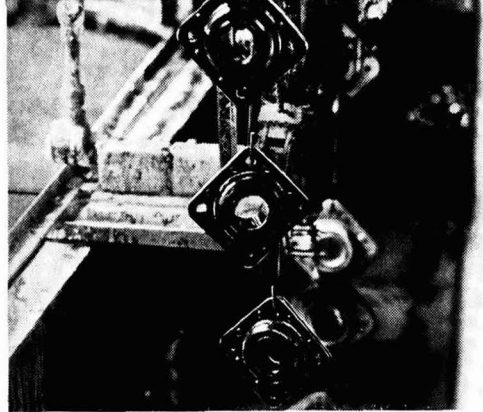
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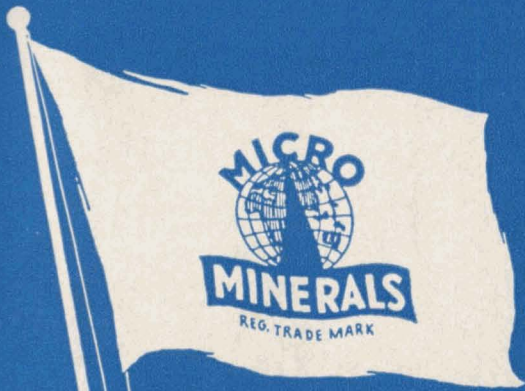
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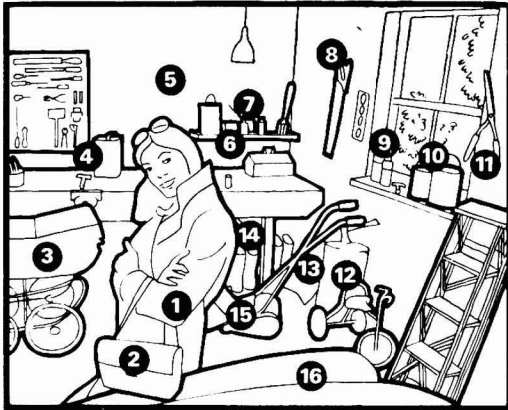
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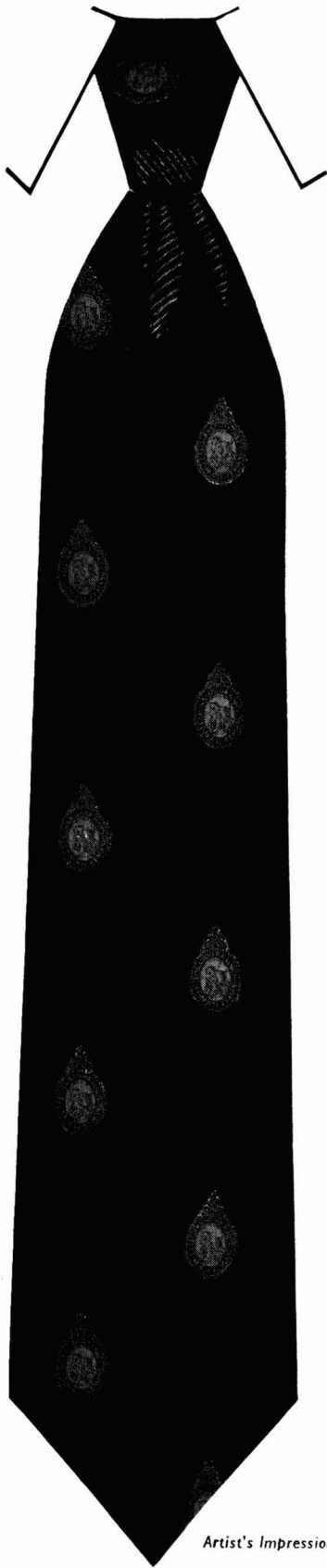
INDEX TO ADVERTISERS



- 1 Methyl ethyl ketone**—vinyl lacquer solvent
- 2 Ethyl amyl ketone**—leather finish solvent
- 3 'Oxitol' glycol ethers**
high boiling components of finish
- 4 Isophorone**—can lining solvent
- 5 'Oxitol' glycol ether esters**
coalescing agents in emulsion paint
- 6 Polyethylene glycols**
printing ink constituents
- 7 'Shellsol' hydrocarbons**
can coating solvents
- 8 Secondary butyl alcohol**
nitrocellulose lacquer solvent
- 9 Diacetone alcohol**—aerosol paint solvent
- 10 Monoethylene glycol**
antifreeze in emulsion paint
- 11 Methyl isobutyl carbinol**
nitrocellulose lacquer solvent
- 12 Methyl isobutyl ketone**
nitrocellulose lacquer solvent
- 13 Isopropyl alcohol**—printing ink solvent
- 14 Toluene**—neoprene adhesive solvent
- 15 Xylene**—stoving paint solvent
- 16 Acetone**—metal finish solvent



A	
Alcoa International SA	viii, ix
Ashby, Morris, Ltd.	Cover
Associated Book Publishers Ltd.	xxxviii
Associated Lead Manufacturers Ltd.	xl
B	
Badische Anilin- & Soda-Fabrik AG	xxix
Bakelite Ltd.	xxxix
Banner, Samuel, & Co. Ltd.	xxvi
Beadel, James, & Co. Ltd.	xli
Berk, F. W., & Co. Ltd.	xxxvii
BIP Chemicals Ltd.	xxxvi
Bray, Conway, Ltd.	ii
British Resin Products Ltd.	xxviii
British Titan Products Co. Ltd.	xxii
C	
Cabot Carbon Ltd.	xiv
Ciba (ARL) Ltd.	xv
<i>Classified Advertisements</i>	xlii, xliii, xliv
Cory, Horace, & Co. Ltd.	xxiv
Crosfield, Joseph, & Sons Ltd.	xxxiv
CSR Chemicals Ltd.	vi
E	
English China Clays Sales Co. Ltd.	vii
G	
Geigy (UK) Ltd.	xxxi
Gilbarco Ltd.	xi
Glovers (Chemicals) Ltd.	xxxv
Golden Valley Colours Ltd.	xvi
Greaves, Joshua, & Sons Ltd.	x
H	
Hardman, E., Son & Co. Ltd.	xxxii
Hercules Powder Co. Ltd.	i
Heydon, Harold, & Co. Ltd.	Cover
I	
ICI Ltd. (Paints and Resins)	v
K	
Keiner & Co. Ltd.	iii
Kronos Titanium Pigments Ltd.	xxxiii
M	
Metchim & Son Ltd.	ii
Mitchell, W. A., & Smith Ltd.	x
Monsanto Europe SA	xii, xiii
N	
Norwegian Talc (UK) Ltd.	xvii
P	
Pascall Engineering Co. Ltd.	xxvi
R	
Resinous Chemicals Ltd.	xxx
S	
Shell Chemicals (UK) Ltd.	xviii-xix, xxv
Shell International Chemical Co. Ltd.	xxvii
U	
United Coke & Chemicals Co. Ltd.	xxi, xxxviii
Y	
Younghusband Stephens & Co. Ltd.	iv



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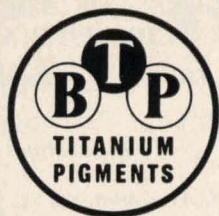
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Contents

Vol. 50 No. 9 September 1967

Transactions and communications

Dispersion	822
<i>G. D. Parfitt</i>	
The adsorption of long chain acids on to rutile from n-heptane	844
<i>R. H. Ottewill and J. M. Tiffany</i>	
Adsorption of polyamides. Infra-red measurements of the interaction with rutile and carbon black surfaces	865
<i>R. H. Schiesser, W. D. Schaeffer and A. C. Zettlemoyer</i>	
<i>Reviews</i>	885
<i>Information received</i>	887
<i>Section proceedings</i>	889
<i>Notes and news</i>	890
<i>Register of members</i>	893

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Interfacial behaviour

Foreword

The 13th Biennial Conference of the Oil and Colour Chemists' Association was held at Scarborough in the period 20-24 June 1967.

At the beginning of his term of office as President, Dr. S. H. Bell initiated an exercise which he called "Forward Thinking." The Hon. Officers, and later the Council and Section Committees, were asked to take a close look at Association activities to ensure that the needs of Members were met, and to consider where modifications and improvements might be made to meet changing conditions, so that the Association retained its proud position.

One such activity that was, and is being, studied is the Biennial Conference.

In the past, conference time has been limited to morning sessions, except for the introduction of the Workshop Sessions at the last conference. Some Members have felt that more conference time should be available, though all have agreed that informal discussion in small groups, often socially, was a valuable feature of these international gatherings. For the 1967 Conference, Council agreed to the introduction of an afternoon session and the retention of the Workshop Sessions.

The President speaking of the Conference said that it "bridged the gap" between the academic and the technological and that was, possibly, the aim of the 1967 Conference.

The experimental afternoon session was no less well attended than the traditional morning ones. Discussion time was, as we have now come to expect, insufficient and the level was excellent. This was no doubt due, in large measure, to the lucid presentation of the fully preprinted papers by their authors.

The Workshop Sessions were well attended and again the bookings of available places by intending participants indicated that these discussion groups will continue. The Convenors, Dr. H. G. Rains, Dr. F. M. Smith and Mr. J. R. Taylor all reported useful interchange of ideas.

Some slight changes were made in the method of running the Conference. The Chairman of the first Session, Dr. G. D. Parfitt, first set the scene with a full lecture on the principles, theories and mechanisms of dispersion and then took the chair for the first and third sessions with Dr. L. Valentine as Chairman for the second and fourth sessions. Both Chairmen summarised each session and linked the theme that ran throughout the Conference. None of this would have been possible without the collaboration of the authors, four from overseas, who prepared, in good time, a series of well-written and valuable contributions to the subject.

The Council of the Association are still considering the future needs of our Conference. It is possible that the pattern will change again in the future but the small changes made in the 1967 Conference were successful and the innovations made will certainly be repeated, though possibly in modified form.

A. T. S. RUDRAM, *Hon. Research and Development Officer*

Dispersion

By G. D. Parfitt

Chemistry Department, University of Nottingham, Nottingham

Summary

Dispersion is discussed as a two stage process, the first, termed dispersibility, being wetting of the pigment by the medium, the second being the stability of the system.

The dependence of the stability of the system on the potential energy caused by the interplay of the attractive (van der Waals) and repulsive forces acting on the particles is cited. A comparison between theoretical and practical aspects of the DLVO theory for stability in relation to repulsive surface charge is made in aqueous and hydrocarbon systems. Non-ionic systems are briefly discussed.

Dispersion

Résumé

On considère le phénomène de dispersion en tant qu'un processus à deux étapes, la première, que l'on appelle dispersibilité, embrasse le mouillage du pigment par le liant, tandis que la deuxième entraîne la stabilité du système.

On mentionne que la stabilité du système se dépend de son énergie potentielle en provenance de l'interaction des forces attractives (van der Waals) et répulsives avec les particules pigmentaires. On compare, dans des systèmes aqueux et d'hydrocarbure, des aspects théoriques et pratiques de la théorie DLVO (double couche de Verwey et Overbeek) à l'égard de stabilité par rapport à la charge répulsive superficielle. On discute brièvement des systèmes nonioniques.

Dispersion

Zusammenfassung

Dispersion wird als ein durch zwei Vorgänge beeinflusster Prozess besprochen, und zwar erstens Dispergierbarkeit, mit Hilfe deren das Pigment vom Bindemittel benetzt wird, zweitens Stabilität des Systems.

Auf die dwoich das Wechselspiel der auf die Partikel einwirkenden anziehenden (von der Waals) und abstossenden Kräfte verwisachte Abhängigkeit der Stabilität des Systems von der Potentialenergie wird hingewiesen. Theoretische und praktische Gesichtspunkte der DLVO Theorie der Stabilität im Verhältnis zur abstossenden Ladung der Oberfläche werden sowohl in wässrigen, als auch in Kohlenwasserstoff-Systemen verglichen. Nicht-Ionensysteme werden Kurz besprochen.

Дисперсия

Резюме

Обсуждается дисперсия как двухступенчатый процесс, первая ступень которого, именуемая дисперсностью, является мочением пигмента средой, тогда как вторая ступень представляет из себя устойчивость системы. Цитируется зависимость стабильности системы от потенциальной энергии, вызываемой взаимодействием сил притяжения (ван-дер-ваальсовских сил) и отталкивающих сил действующих на частицы. Производится сравнение между теоретическими и практическими аспектами теории устойчивости Держагуина-Ландауа-Вервейя-Овербика по отношению к отталкивающему поверхностному заряду в водных и углеводородных системах. Дается краткое обсуждение неионных систем.

The term *dispersion* is used here to refer to the complete process of incorporating a pigment into a liquid vehicle such that the final product consists of fine particles distributed throughout the medium. In an attempt to understand the relevance to dispersion of the various parameters associated with any particular solid-liquid system, it is useful to distinguish basically two stages in the process, these being quite distinct in their nature but overlapping in practice.

The first involves the displacement of air from the pigment by the medium (wetting), and usually requires mechanical work for its completion ; the ease with which this stage can be brought about is termed *dispersibility*. Once dispersed, there is a natural tendency for the particles to re-aggregate, and the *stability* of the system represents the second stage in the overall process of dispersion. Assessing the relative contribution of the two effects to the state of the final dispersion is often difficult experimentally because of their individual complexity and that associated with the overlap. However, as separate phenomena, the principles involved in each are fairly well established.

Dispersibility

In many practical uses of pigments, the primary particle size is sufficiently small for further sub-division to be unnecessary. The dry pigment, however, usually contains some *aggregates* of primary particles and these may be attached to other aggregates and/or primary particles forming *agglomerates*.* Aggregates may require considerable energy to break them down completely, to a point where the surface of each primary particle is available to the wetting liquid. The aggregates and agglomerates arise for various reasons which may be concerned with either the manufacture or storage conditions or both, and a knowledge of the factors governing their nature and strength is essential to a study of the dispersibility of any particular system.

The first part of the dispersion process involves the displacement of air and any other adsorbed species from the external surface of the powder and also from the small channels inside and between the aggregates and agglomerates. Once the air has been displaced, separation of the agglomerates into aggregates and/or primary particles is then possible, given the appropriate mechanical treatment. It then remains to disperse the particles (of various sizes and structure) throughout the medium to effect a permanent, or otherwise, separation.

Wetting of a solid by a liquid is normally described in terms of the *equilibrium contact angle* θ and the appropriate interfacial tensions as shown in Fig. 1.

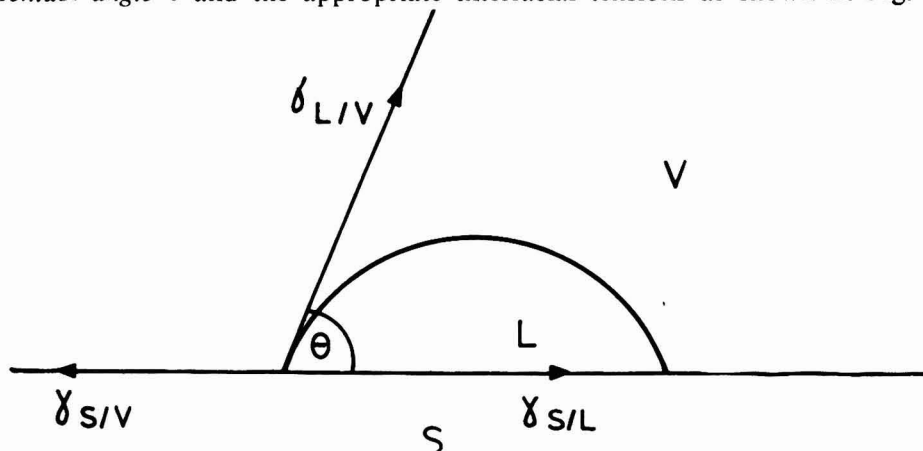


Fig. 1. Forces acting on a drop resting on a solid surface

*The terminology used here follows that proposed by Gerstner¹ in 1966. The surface area of an aggregate is less than the total area of the constituent primary particles ; that of an agglomerate is the same.

At equilibrium, equating the forces leads to Young's equation,

$$\gamma_{S/V} = \gamma_{S/L} + \gamma_{L/V} \cos \theta, \dots\dots\dots (1)$$

where $\gamma_{S/V}$, $\gamma_{S/L}$ and $\gamma_{L/V}$ are the interfacial tensions at the solid/vapour, solid/liquid and liquid/vapour interfaces respectively. In all cases the vapour refers to that of the liquid, i.e., the system is at equilibrium with the vapour at its saturated vapour pressure. It is important to remember that Young's equation only applies to a system at equilibrium and for which $\gamma_{L/V}$ and θ are given their equilibrium values.² For practical purposes, a liquid does not wet a solid when $\theta > 90^\circ$, although strictly speaking a zero contact angle signifies wetting and the complete and spontaneous displacement of air from the surface. From equation (1)

$$\cos \theta = \frac{\gamma_{S/V} - \gamma_{S/L}}{\gamma_{L/V}} \dots\dots\dots (2)$$

from which it is apparent that if $\theta < 90^\circ$, a decrease in $\gamma_{L/V}$ will reduce θ and hence improve the wetting. The addition of a surface active agent causes a reduction in $\gamma_{L/V}$ and, if adsorbed, a change (probably a decrease) in $\gamma_{S/L}$, both effects leading to better wetting. The change in $\gamma_{S/V}$ is probably negligible in most cases ; the dominating factor in wetting is normally $\gamma_{L/V}$.

The work W_d involved in the wetting of 1 cm² of the external surface of a powder by a liquid is given by the difference between the interfacial energies before and after wetting

$$W_d = \gamma_{S/L} - \gamma_{S/V} \dots\dots\dots (3)$$

$\gamma_{S/V}$ is the surface tension of the solid in equilibrium with the vapour of the liquid and, following Patton³, W_d is termed the work of dispersion. It is useful, as Patton points out, to break down the overall process into three stages using a 1 cm cube to illustrate the principles involved. Patton calls the stages adhesion, immersion and spreading, and in Fig. 2 these are represented by the changes

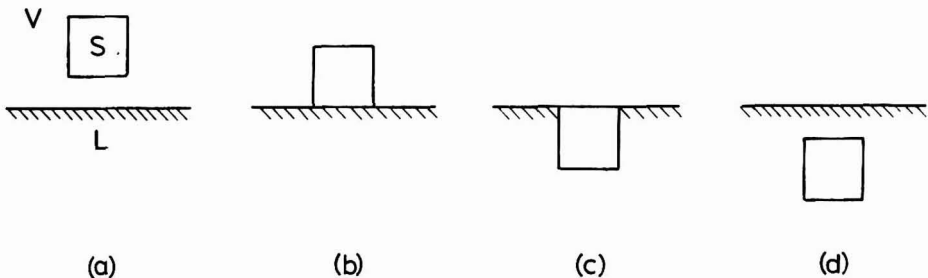


Fig. 2. The three stages involved in the complete wetting of a solid cube by a liquid: (a) to (b) adhesion, (b) to (c) immersion, (c) to (d) spreading.

from (a) to (b), (b) to (c) and (c) to (d) respectively ; (a) to (d) represents complete wetting. The energy changes that take place are given in terms of both the interfacial energies and, using Young's equation, the contact angles by

work of adhesion $W_a = \gamma_{S/L} - (\gamma_{L/V} + \gamma_{S/V}) = -\gamma_{L/V} (\cos \theta + 1) \dots\dots (4)$

work of immersion $W_i = 4\gamma_{S/L} - 4\gamma_{S/V} = -4\gamma_{L/V} \cos \theta \dots\dots\dots (5)$

work of spreading $W_s = (\gamma_{S/L} + \gamma_{L/V}) - \gamma_{S/V} = -\gamma_{L/V} (\cos \theta - 1) \dots (6)$

For the entire process

$$W_d = W_a + W_i + W_s = 6\gamma_{S/L} - 6\gamma_{S/V} = -6\gamma_{L/V} \cos \theta \dots\dots\dots (7)$$

which, put on a unit area basis, is the same as equation (3). By using Young's equation only the equilibrium values of $\gamma_{L/V}$ and θ are applicable to equations (4) to (6). Furthermore, we have assumed the surface of the solid before wetting to be in equilibrium with the vapour of the liquid, i.e., there is an adsorbed film of liquid molecules on the surface. This conforms with Young's equation. Hence, for the wetting of a surface free of liquid molecules, which is in equilibrium with its own vapour, an extra energy must be considered, being that associated with the adsorbed molecules, and this may be substantial.^{4,5}

Bearing in mind these factors we may, with values of the two measurable quantities θ and $\gamma_{L/V}$, use the equations to predict whether or not any particular stage of the process is spontaneous, i.e., when the appropriate W is negative. If W is positive, then work must be expended on the system for the process to take place. The conclusions are

- (a) the adhesion process is invariably spontaneous,
- (b) spontaneous immersion takes place only when $\theta < 90^\circ$,
- (c) spontaneous spreading takes place only when $\theta = 0$,

and (d) spontaneous dispersion occurs only when $\theta < 90^\circ$.

In practice θ is often close to zero and hence spontaneous dispersion is common. Such is the ideal case, without reference to surface heterogeneity (both chemical and physical), advancing and receding contact angles etc., all of which may help to confuse the picture.

The penetration of the liquid into the channels between and inside the agglomerates is more difficult to define precisely. To force into a tube of radius r a liquid which makes a contact angle θ with the walls, a pressure P is required such that

$$P = -2\gamma_{L/V} \cos \theta / r \dots\dots\dots (8)$$

Hence, the penetration of the liquid is only spontaneous when $\theta < 90^\circ$. Substituting Young's equation into equation (8) gives

$$P = -2(\gamma_{S/V} - \gamma_{S/L}) / r \dots\dots\dots (9)$$

which shows that now the requirement is to make $\gamma_{S/L}$ as small as possible since $\gamma_{S,V}$ is a constant. The relationship between P and $\gamma_{L/V}$ is illustrated in Fig. 3.

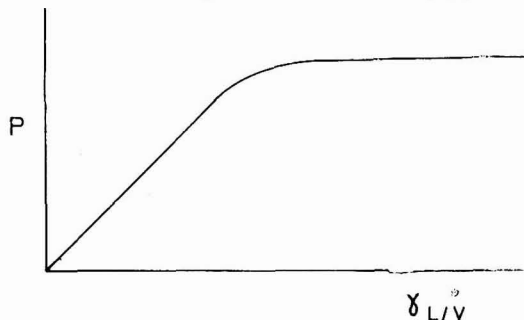


Fig. 3. The pressure required to force a liquid into a capillary as a function of the surface tension of the liquid

When θ is zero, P is directly proportional to $\gamma_{L/V}$, so that a large $\gamma_{L/V}$ is desirable. Ultimately, changes in θ accompany the increase in $\gamma_{L/V}$, and, assuming the only variable tension to be $\gamma_{L/V}$, P will remain constant (from equations (2) and (8)) and the limiting value increases proportionally with $(\gamma_{S/V} - \gamma_{S/L})$. Hence, it is desirable to maximise $(\gamma_{S/V} - \gamma_{S/L})$ and to keep $\gamma_{L/V}$ as small as possible ; normally a surface active agent affects both $\gamma_{L/V}$ and $\gamma_{S/L}$.

The rate of penetration of liquid into the tube follows the Washburn equation⁶

$$\frac{dl}{dt} = \frac{r\gamma_{L/V}}{4\eta l} \cos \theta \dots\dots\dots (10)$$

where l is the depth of penetration in time t and η the viscosity of the liquid. Rapid penetration is assisted, therefore, by high $\gamma_{L/V} \cos \theta$, low θ and low η , and by a loosely packed pigment (r as large as possible). High $\gamma_{L/V}$ and low θ are normally incompatible ; a low contact angle is certainly very important. On integration, equation (10) becomes

$$\frac{l^2}{t} = \frac{r\gamma_{L/V} \cos \theta}{2\eta} \dots\dots\dots(11)$$

which may be modified for application to a powder by multiplying l by a tortuosity factor k to allow for the "capillaries" of random shape and size, giving

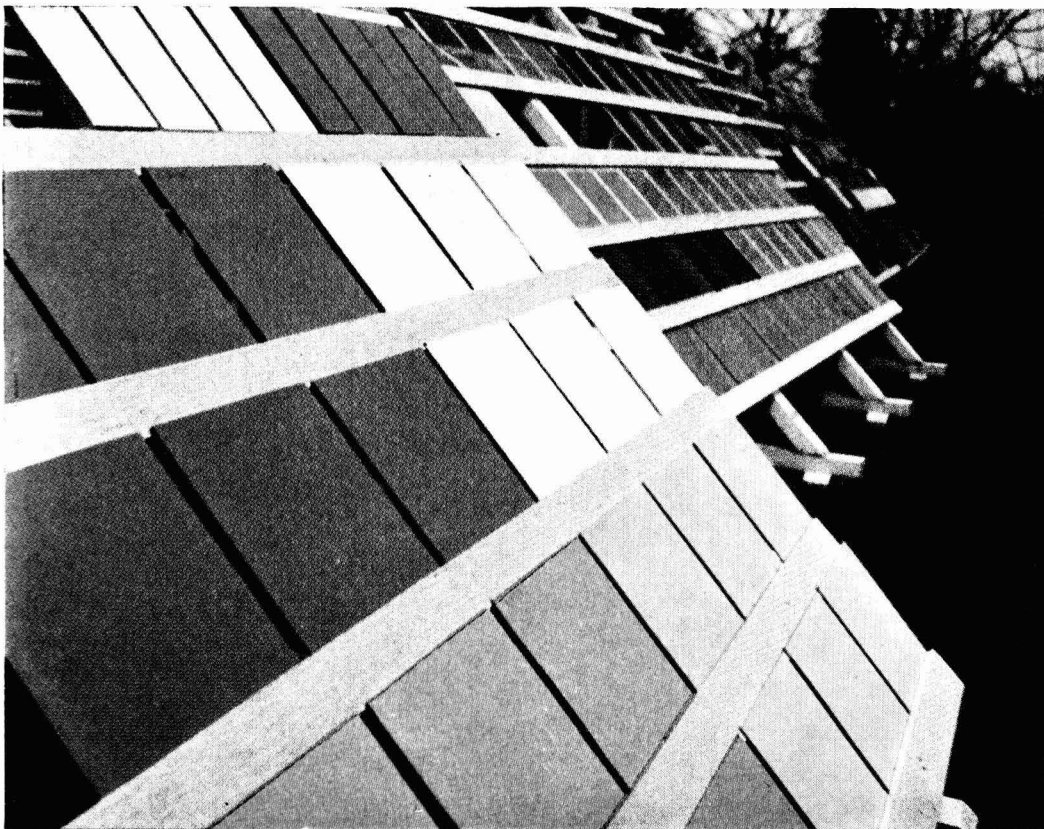
$$\frac{l^2}{t} = \frac{r}{k^2} \frac{\gamma_{L/V} \cos \theta}{2\eta} \dots\dots\dots(12)$$

Equation (12) forms the basis of one of the methods⁷ which has been used for the measurement of θ for a powder-liquid system, which clearly, from what has been said, is an important parameter to evaluate. A known weight of dried powder is packed in a glass tube (of about 1 cm internal diameter) one end of which is dipped in the liquid, and the rate of rise of the liquid measured.

A plot of l^2 against t is usually linear (Fig. 4), the slope depending only on the nature of the liquid, assuming constant packing characteristics. Using a liquid known to have zero contact angle with the solid under investigation, the slope leads to a value of (r/k^2) , hence θ for other liquids. This and other methods for the determination of θ for powders have been reviewed.^{8,9} Each method is subject to criticism, which is often severe ; in the flow method a major problem arises when there are changes in particle packing on contact with the liquid, which invalidates the measurement. Nevertheless, qualitative observations of flow rate are possible for comparison purposes and, as such, may be relevant to an overall study of dispersibility.

In summary, dispersibility is dependent on

- (a) the energy associated with the wetting of the external surface,
- (b) the pressure involved in the liquid penetrating inside and between the agglomerates, and
- (c) the rate of penetration of liquid into the pigment.



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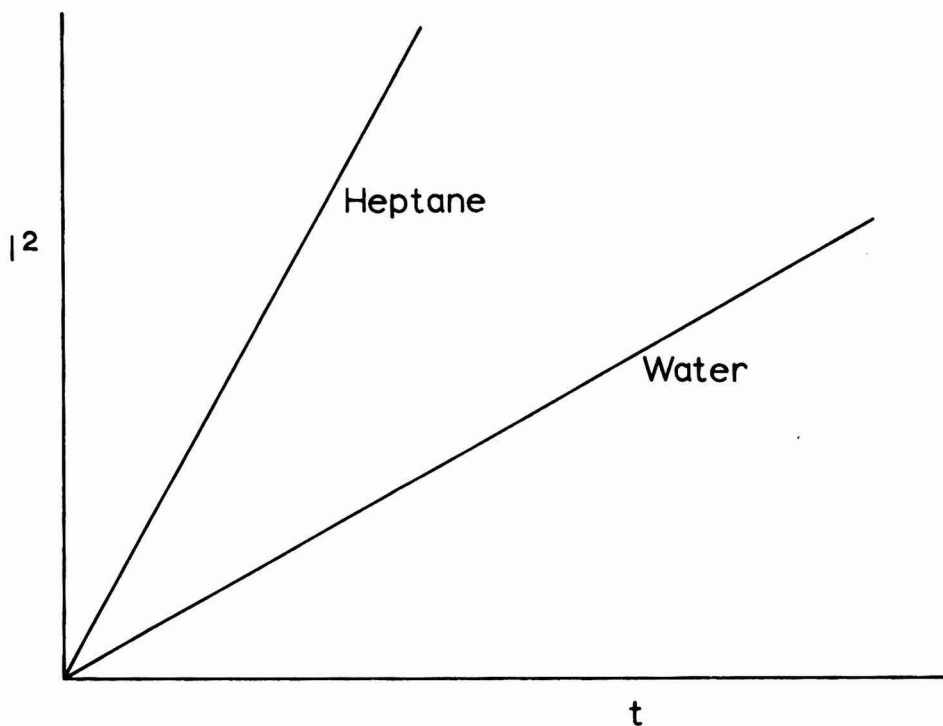


Fig. 4. The relationship between l^2 and t in the case of water and heptane penetrating on oxide powder

All these are related to the contact angle θ and the surface tension of the liquid $\gamma_{L/V}$. In general, the process is likely to be more spontaneous the lower θ and the higher $\gamma_{L/V}$, although these two factors tend to operate in opposite senses. Certainly a low θ is an important requisite. In addition to the wetting phenomena, there is the question of the amount of mechanical energy required to bring about a desired state of dispersion, which depends on the strength of attachment of particles in the aggregates and agglomerates. Surface active agents are known to assist in the break-down by mechanical means of aggregates and primary particles. This is the Reh binder effect.¹⁰

Surprisingly little work of a fundamental nature has been reported on the relationship between dispersibility and the various parameters involved. In our laboratory we are studying the dispersibility of carbon blacks and rutile in aqueous solutions of surface active agents. The relationship between wetting and dispersibility of Graphon (graphitised Spheron 6) is illustrated in Figs. 5 and 6. Following end-over-end shaking with dodecyl trimethylammonium bromide at about 20 revolutions per minute for two hours and allowing the tubes to stand for eighteen hours, it is observed (Fig. 5) that a marked increase in the quantity of carbon remaining dispersed occurs at a concentration below the critical micelle concentration of 16 mM. Comparison with the adsorption isotherm shows that this concentration does not correspond to any obvious change in the nature of

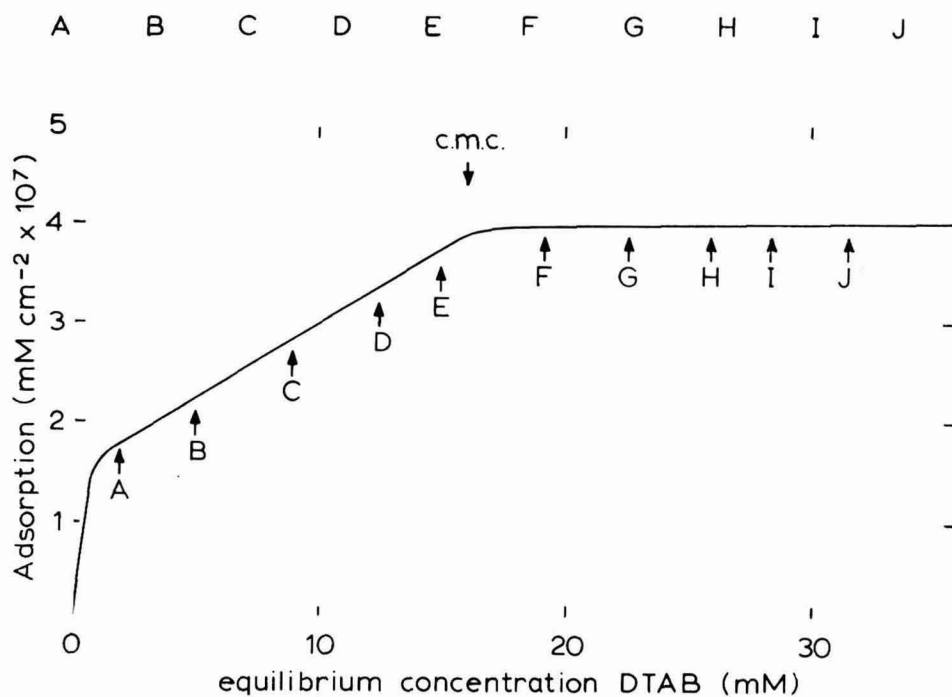
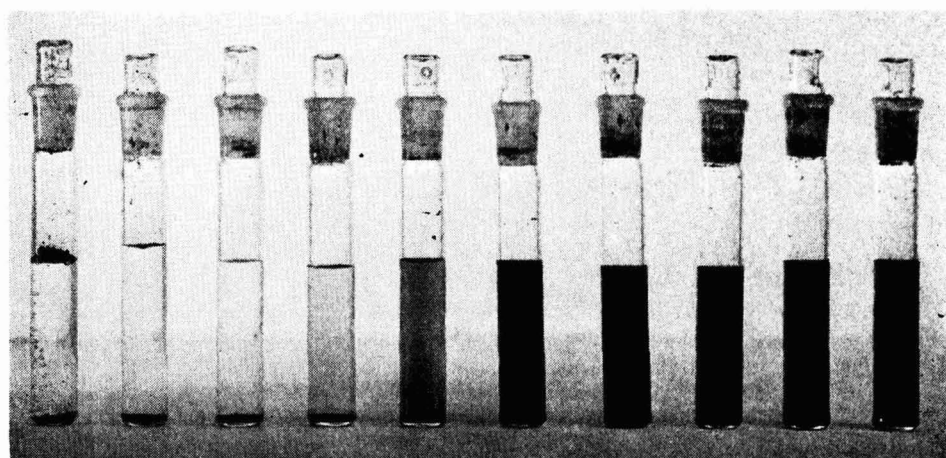
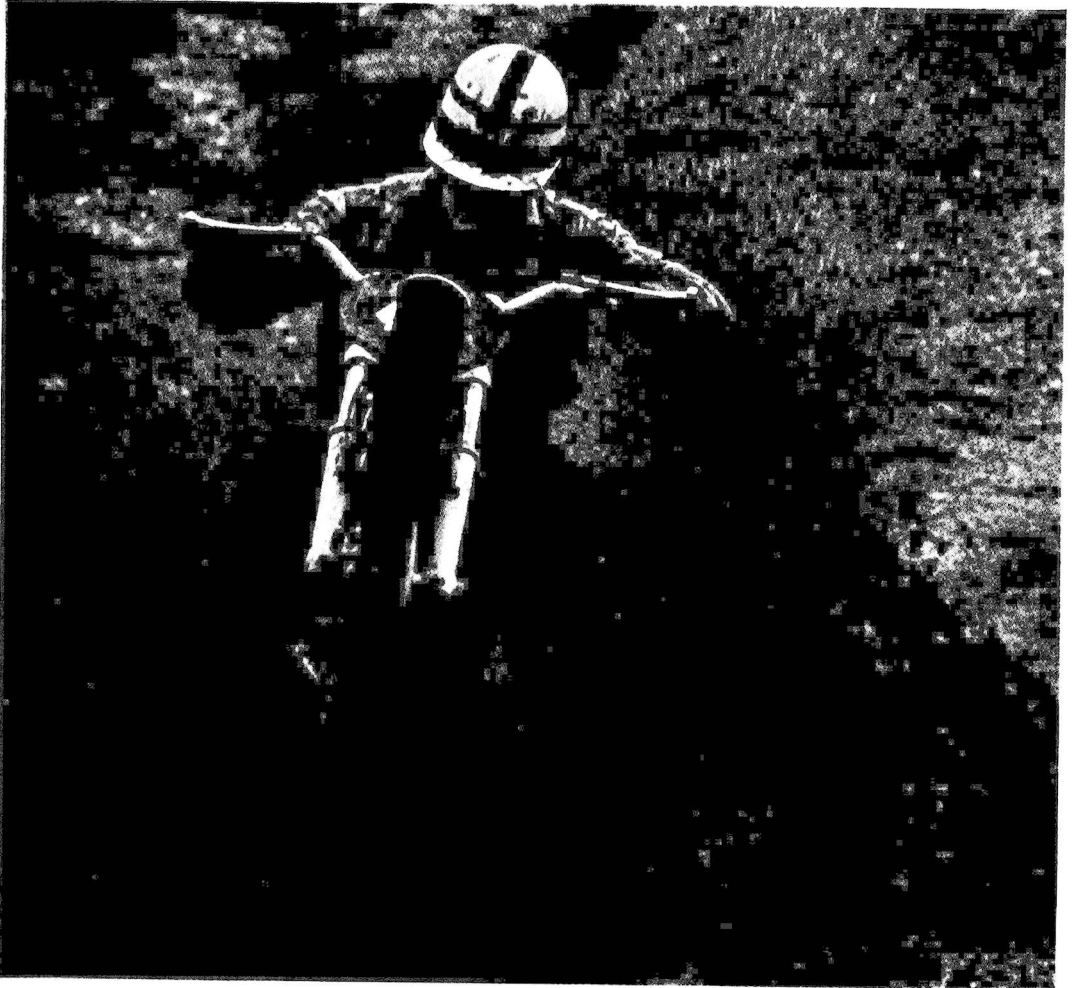


Fig. 5. The relationship between the dispersibility of Graphon in aqueous solutions of dodecyl trimethylammonium bromide and the adsorption isotherm, c.m.c. = critical micelle concentration

the adsorbed layer. To put the changes on a more quantitative basis, we have measured the optical density of the dispersions. Fig. 6 shows the plots of optical density against concentration of, in this case, sodium dodecyl sulphate, and includes experiments carried out in solutions of different ionic strength; changes in the latter would be expected to have a profound effect if the surface charge is relevant to the process. In fact, for both the cationic and anionic agents, the



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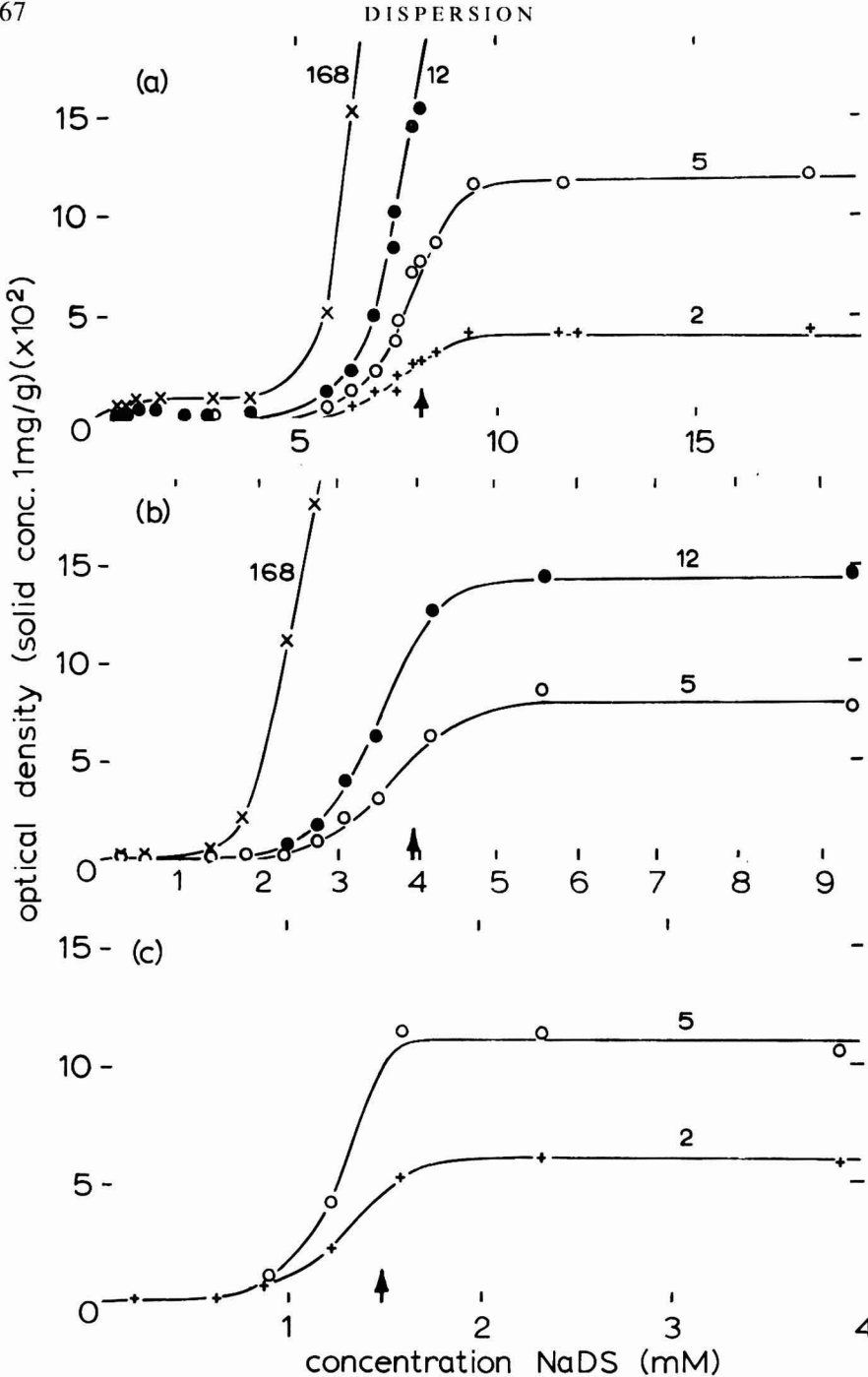


Fig. 6. The dispersibility of Graphon in aqueous solutions of sodium dodecyl sulphate with and without NaCl, shown as values of optical density put on a standard weight basis: (a) without NaCl, (b) with 0.02 M NaCl, (c) with 0.1 M NaCl. The numbers indicate the number of hours subjected to end-over-end action. The arrows indicate the critical micelle concentrations

change in dispersibility is directly related to the concentration of adsorbed surface active ions in the surface layer, and not to surface charge density and surface potential on which the stability of the resulting dispersion depends. Preliminary experiments using the Bickerman method¹¹ for measuring θ , shows that the marked increase in dispersibility occurs when θ becomes $< 90^\circ$, for solutions with and without added salt. In these experiments, the mechanical energy is small, so that most of the dispersing action is associated with the wetting phenomena.

Stability

In the context of the present discussion, the term stability is associated with the process, commonly called *flocculation*, in which the total number of particles decreases with time as a result of collisions leading to clusters (floculates) of aggregates and/or primary particles.* Whether or not a particular system is defined as *stable* is to some extent arbitrary since it depends on the time scale over which observations are made. Normally, the stability is related to the height of a potential energy barrier which exists between the particles, and is similar in principle to the activation energy in chemical kinetics. This barrier arises from the interplay of two forces, one being attractive (van der Waals) and the other repulsive due to surface charge, adsorbed layers, etc. For a stable system, i.e., when there is no change in particle number and size with time, this barrier must be at least *ca.* 20 times the thermal energy of the particles.

In many cases, a surface active agent is necessary for stability, and the adsorption of this material may give rise to a surface charge, or to a non-ionic adsorbed layer such that steric or entropic factors predominate. In either case, it is necessary to understand the chemical and physical nature of the adsorbed layer, which means that measurement of adsorption from solution and the characterisation of the solid surface are fundamental experiments. The existence of a relationship between adsorption and stability is a very important question.

When two colloidal particles approach each other, the attractive force increases with decreasing inter-particle distance, and has a range comparable with the size of the particles. For two spheres of radius a and distance between centres of R , the potential energy of attraction V_A is given by¹³

$$V_A = -\frac{A}{6} \left[\frac{2}{S^2 - 4} + \frac{2}{S^2} + \log_e \frac{(S^2 - 4)}{S^2} \right] \dots\dots\dots (13)$$

where $S = R/a$. A is the Hamaker constant, the value of which depends on the nature of the material of the particles and the medium separating them; it may also be modified by an adsorbed layer, as will be mentioned again later. It is possible to calculate a value for A from optical data for any particular system,¹⁴ and hence to derive a plot of V_A against distance between particles.

In the absence of a repulsive force, rapid flocculation occurs, for which the

*It seems that most of the readers of this *Journal* use the term flocculation to describe this process. However, in other contexts, *coagulation* is used and some authors use both indiscriminately. There is some justification for differentiating between them¹² but this is by no means universally accepted.

theory was proposed by Smoluchowski.¹⁵ The rate of flocculation, i.e., the rate of decrease of the total number of particles, is given by

$$dN/dt = k'N^2 \dots\dots\dots (14)$$

where N is the number of particles per cm^3 at time t , and k' is the rate constant. For rapid flocculation, $k'_o = 8\pi Da$, where D is the particle diffusion coefficient given by the Einstein equation $D = kT/6\pi\eta a$ for a liquid of viscosity η (k is the Boltzmann constant). It is obvious that, for particle concentrations of the order of those found in practical systems, flocculation would be rapid, hence the need for a repulsive force.

Interaction between particles having an electrical double layer

For the case of particles for which the repulsive force is associated solely with the surface charge and related effects, a theory of stability has been proposed by Deryaguin and Landau¹⁶ in the Soviet Union, and independently by Verwey and Overbeek¹⁷ in the Netherlands. It is now commonly called the DLVO theory and, in principle, applies to dispersions in both aqueous and non-aqueous media. The theory involves an estimation of the relative magnitudes of the attractive and repulsive forces as a function of the relevant parameters. The repulsive force arises from the overlap, as the particles approach each other, of the electrical double layers associated with the particles. Fig. 7 shows how the electric potential decays with distance from a surface of potential ψ_o . The inner region of the double layer at close distances, over which the potential decays to ψ_δ , includes any adsorbed ions; it is the Stern layer. From distance δ into the bulk solution where $\psi = 0$, the potential decays exponentially through the diffuse part of the double layer, the Gouy layer. The potential at the plane of shear, the zeta potential ζ , is readily measured by an electrokinetic measurement and electrophoresis is commonly employed. Neither ψ_δ or ψ_o are obtainable by experiment and it is normal to use ζ as equivalent to the surface potential which is relevant to stability theory, i.e., the potential which controls the decay in potential at larger distances from the surface when overlap of the double layers occurs. Double layers are often described in terms of their "thickness" which, although only a theoretical concept, is of great value in defining the system. A plane at a distance $1/\kappa$ from the surface is assumed to contain all the ions of the diffuse part of the double layer, and this distance is the hypothetical "thickness of the double layer." For a 0.1M aqueous solution of monovalent ions at 25°C the value of $1/\kappa$ is approximately 10Å, while for a hydrocarbon solution of a surface active agent such as Aerosol OT, the ionic concentration is *ca.* 10^{-11}M and the thickness is *ca.* 15 microns. Hence, in using the double layer overlap theory with 0.1M aqueous solutions, it would be necessary to have a clear understanding of the nature of the interfacial region, but this would be of less importance in the non-aqueous case (unless there were other complications such as adsorbed water on an oxide surface).¹⁸⁻²⁰ A major advantage with non-aqueous systems is that, since the potential decays so slowly from the surface, the zeta potential is an excellent substitute for the surface potential; this may not be so for aqueous systems (yet to be adequately justified.)

Various equations have been proposed for the repulsive potential energy, but here we shall only mention two, both of which were derived for spherical

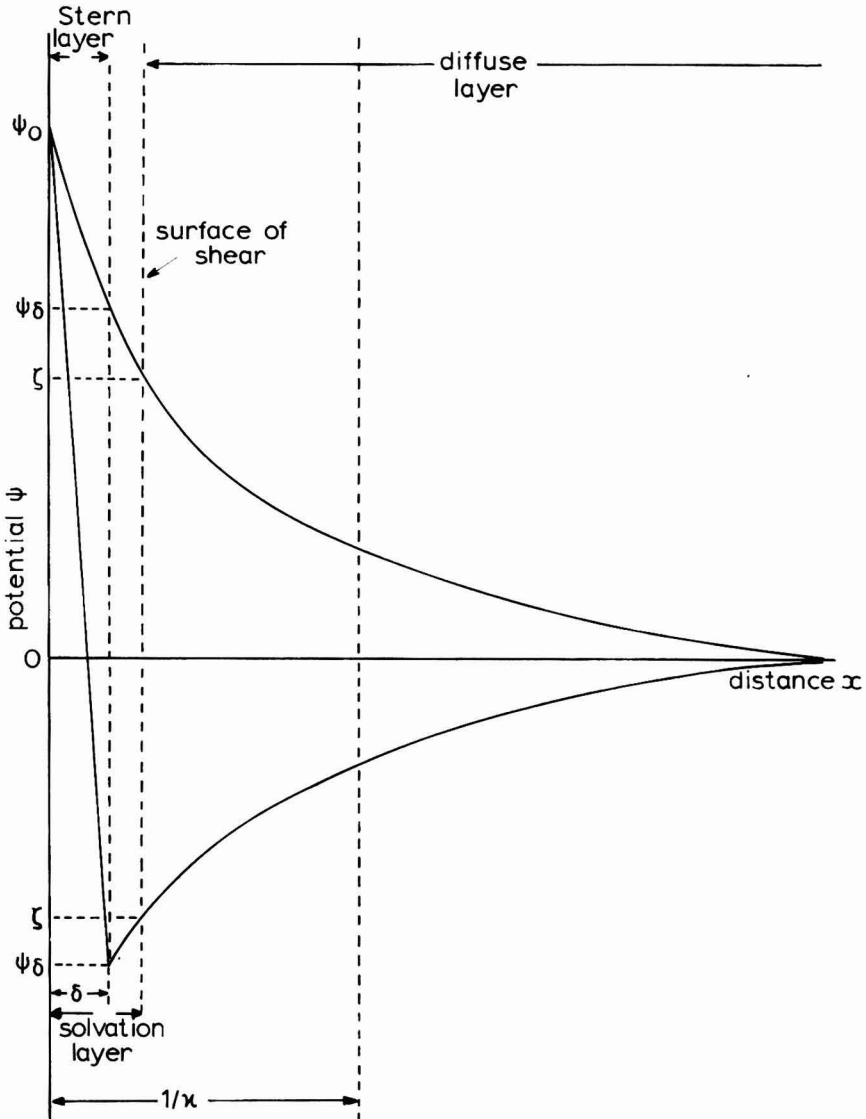


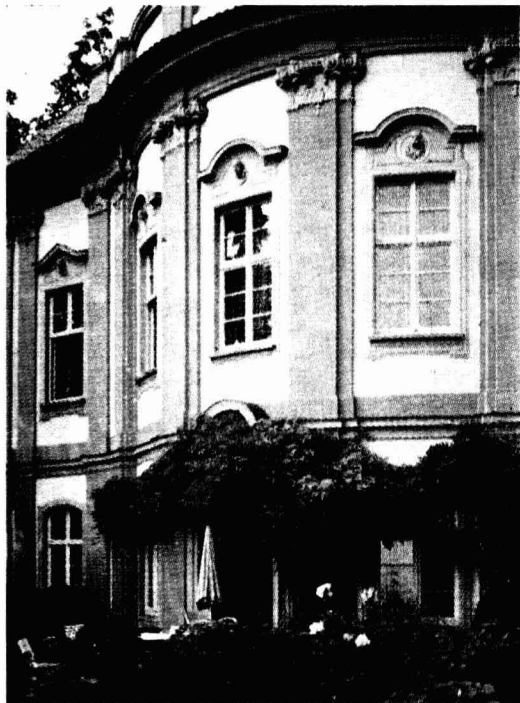
Fig. 7. Potential decay curves for an electrical double layer associated with a colloidal particle whose surface potential is ψ_0 . The lower curve represents strong adsorption in the Stern layer particles and small ψ_0 . For systems in which $\kappa a \gg 1$ (large particles in aqueous systems with moderate electrolyte concentration)

$$V_R = \frac{\epsilon a \psi_0^2}{2} \log_e (1 + \exp (-\kappa H)) \dots\dots\dots (15)$$

and for $\kappa a \ll 1$ (small particles in non-aqueous systems or in aqueous systems with very low electrolyte concentration).

$$V_R = \frac{\epsilon a \psi_0^2}{H + 2a} \beta \exp (-\kappa H) \dots\dots\dots (16)$$

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In these equations, H is the closest distance between particle surfaces, ϵ the dielectric constant and β a factor to allow for loss of spherical symmetry in the double layers as they overlap (β is defined in Verwey and Overbeek's book¹⁷). For the treatment of the intermediate region of κa , and for higher potentials, the reader is referred to the original literature. In these cases, the mathematics is more complex; fortunately equations (15) and (16) are applicable, in principle, to many practical systems.

The total potential energy V_{tot} for the system is given by the sum of the attractive and repulsive energies, and the form of the resulting potential energy versus distance relationship will be dependent upon the relative magnitudes of the two forces. V_R decreases exponentially with distance, while V_A shows an approximate inverse relationship with the square of the distance. At very small distances attraction predominates, otherwise the form of the V_{tot} versus distance plot depends to a large extent on the repulsive energy term. Fig. 8 illustrates the type of plot we might expect for particles of radius 0.1-1 micron

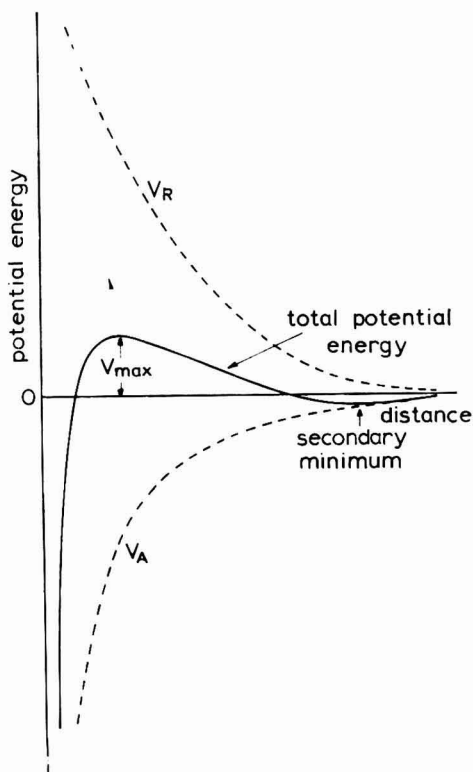


Fig. 8. Potential energy curves for the interaction of two charged surfaces

in an aqueous system containing *ca.* 0.01M electrolyte, for which the range of the attractive and repulsive forces are similar. The effect of reducing the electrolyte concentration (increasing $1/\kappa$ at constant ψ_0) on the total potential

energy curve is shown in Fig. 9; this illustrates the difference between the behaviour in an aqueous and a non-aqueous solution of a surface active agent of the same stoichiometric concentration, e.g. Aerosol OT, which dissolves in both water and hydrocarbons, but ionises to very different extents in the two solvents. When $1/\kappa$ is large, the range of V_R is considerably greater than that of V_A , and the precision of values of the latter becomes less important.

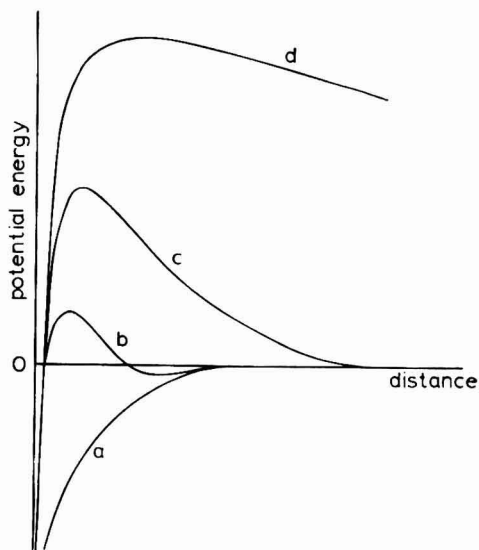


Fig. 9. The influence of electrolyte concentration on the total potential energy of interaction of two spherical particles of radius 1000\AA in aqueous media. $1/\kappa = 10^{-7}$ cm (a), 10^{-6} cm (b), 10^{-5} cm (c), 10^{-4} cm (d)

The effect of increasing the electrolyte concentration on the stability of a colloidal dispersion has been known for a considerable time and has been well documented experimentally. The valency of the added ions is of great relevance (the Schulze-Hardy rule). In aqueous (but not hydrocarbon) systems, the addition of electrolyte and consequent reduction in V_{max} may lead to a minimum in the potential energy curve at larger distances (the secondary minimum, Fig. 8). Although V_{max} may be significant, if the depth of the secondary minimum is sufficiently great (of the order of at least five times the thermal energy of the particles) then the system will flocculate. We might expect that less energy would be required to redisperse such a flocculated system than with one for which there is no secondary minimum. Such a situation gives rise to thixotropy²¹.

The energy relationships tell us whether or not we might expect a system to be "stable," but give no information on the rate of flocculation. A useful way to describe the time effects is in terms of W , the stability ratio, which is a measure of the rate of flocculation relative to that which would obtain if no repulsive energy existed, i.e. rapid flocculation. In terms of the rate constants for flocculation, the stability ratio is given by $W = k'_0/k'$ (c.f. equation (14)). Experimental values of W may be obtained from measurements of particle concentration with time. Such experiments were carried out in our

laboratory by Dr. Lewis, supported by the OCCA Fellowship¹⁴. Theoretically W may be evaluated from the potential energy relationships using the theory of slow flocculation originally proposed by Fuchs²². The expression for W is²³

$$W = \frac{\int_0^{\infty} \exp(V_{tot}/kT) \dots \dots \dots (17)}{\int_0^{\infty} \exp(V_A/kT)}$$

so that $W=1$ when $V_{tot}=V_A$ at all distances. Plots of $\log_{10}W$ (from equation (17)) versus ψ_0 and V_{max}/kT are given in Fig. 10, for particles of various radii in hydrocarbon media for which equation (16) applies²⁴. Particle size is clearly a very important factor. To put the rate on a time basis involves the particle concentration, and is best represented as the half-life of a dispersion (as in chemical kinetics) for which values are readily calculable²⁴.

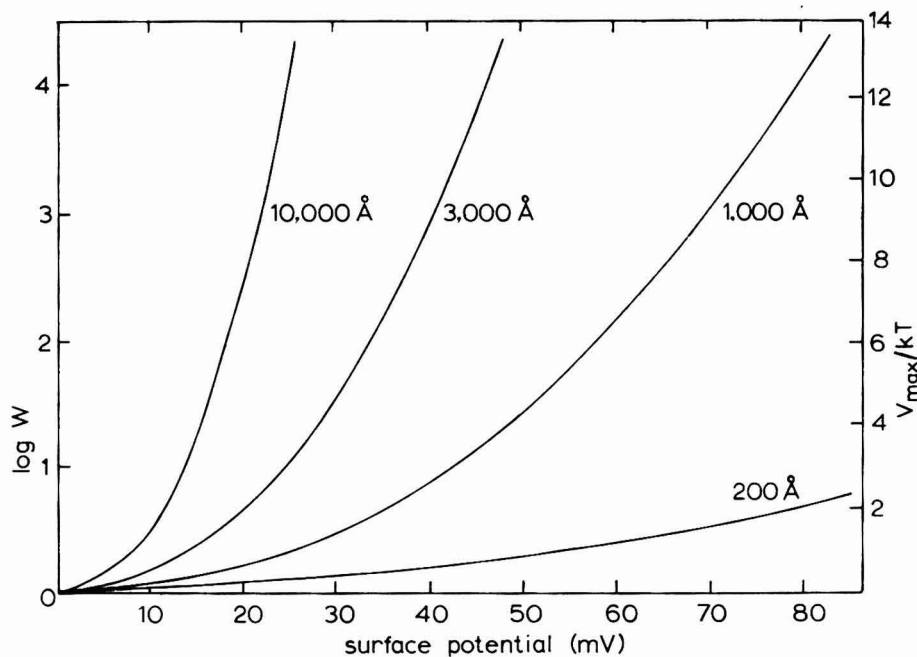


Fig. 10. Theoretical curves of stability ratio against surface potential and potential energy maximum for various particle radii. $A = 5 \times 10^{-13}$ erg

Many experimental facts support the basic premises of the theory, although it will probably need refining in certain respects as more reliable data become available. Certain difficulties, usually quite serious in aqueous systems, arise when theory and practice are compared. In particular, there is the evaluation of the surface potential and of the Hamaker attraction constant; the zeta potential, readily obtainable from electrophoresis experiments, is often used with some success and the Hamaker constant can be estimated from optical data. However, although a fair amount of effort has been directed at aqueous

systems, there remains a number of problems which leave a detailed correlation somewhat unsatisfactory. Nevertheless the DLVO theory still provides an extremely useful basis on which to work. A further factor, which is receiving increasing attention for aqueous systems, is the part played by the solvent layer around the particles. If its removal for particles to come close enough together to form a stable cluster requires extra work, then this constitutes an additional repulsive force. It is still too early to estimate the magnitude of this force although the existence of solvation layers of considerable thickness has been established for aqueous systems by Deryaguin²⁵. In hydrocarbon systems containing very few ions, the zeta potential provides an excellent measure of the surface potential; also the attractive force plays a much less important part in the overall interaction so that an error in the estimation of the Hamaker constant is of little consequence. Hence, for dispersions in hydrocarbons, these two difficulties do not arise and the DLVO theory seems, from our recent experiments with rutile¹⁹ and carbon black¹⁴, to provide a quantitative explanation for the stability characteristics. But other problems arise in such systems, the most serious being trace water, and it is only in absence of these that the behaviour of a particular system may be successfully predicted by the theory.

It is often remarked that practical systems "do not contain monodisperse spheres in solutions containing simple 1 : 1 electrolytes," and of course this is quite true. Present theory should not, however, be disregarded on this basis. For a system containing one pigment only, the deviation from monodispersity and spherical geometry may be effectively small enough so that an appreciable error is not involved when the theory is applied. When more than one pigment is present the situation is naturally more complex. A theory of *heterocoagulation** was proposed originally by Deryaguin²⁶, but a more recent treatment²⁷ is mathematically simpler and may be used for aqueous systems (when $\kappa a > 5$) containing particles with surface potential < 50 - 60 mV (use the zeta potential to a good first approximation). The potential energy of repulsion for two particles of radii a_1 and a_2 and potentials ψ_{01} and ψ_{02} is given by

$$V_A = \frac{\epsilon a_1 a_2 (\psi_{01}^2 + \psi_{02}^2)}{4(a_1 + a_2)} \left[\frac{2\psi_{01} + \psi_{02}}{(\psi_{01}^2 + \psi_{02}^2)} \log_e \left(\frac{1 + \exp(-\kappa H)}{1 - \exp(-\kappa H)} \right) + \log_e (1 - \exp(-2\kappa H)) \right] \dots\dots\dots (18)$$

which becomes equation (15) when $a_1 = a_2$ and $\psi_{01} = \psi_{02}$. Calculations using equation (18) and designed to illustrate the effect of variations in radius and potential are shown in Figs. 11 and 12. Two facts emerge from the theory:

- (a) the particles with the lower radius and potential control the energetics of the flocculation process, and
- (b) although the different particles may have the same sign of surface charge and potential they can nevertheless attract each other during flocculation. This is a consequence of the changes in the surface charge and double layers as the particles approach each other. (See Bierman³⁰.)

*This is the term used originally by Deryaguin. Co-flocculation²⁸ mutual coagulation²⁷ and mutual flocculation²⁹ have also been used—perhaps heteroflocculation would be more appropriate in the present case.

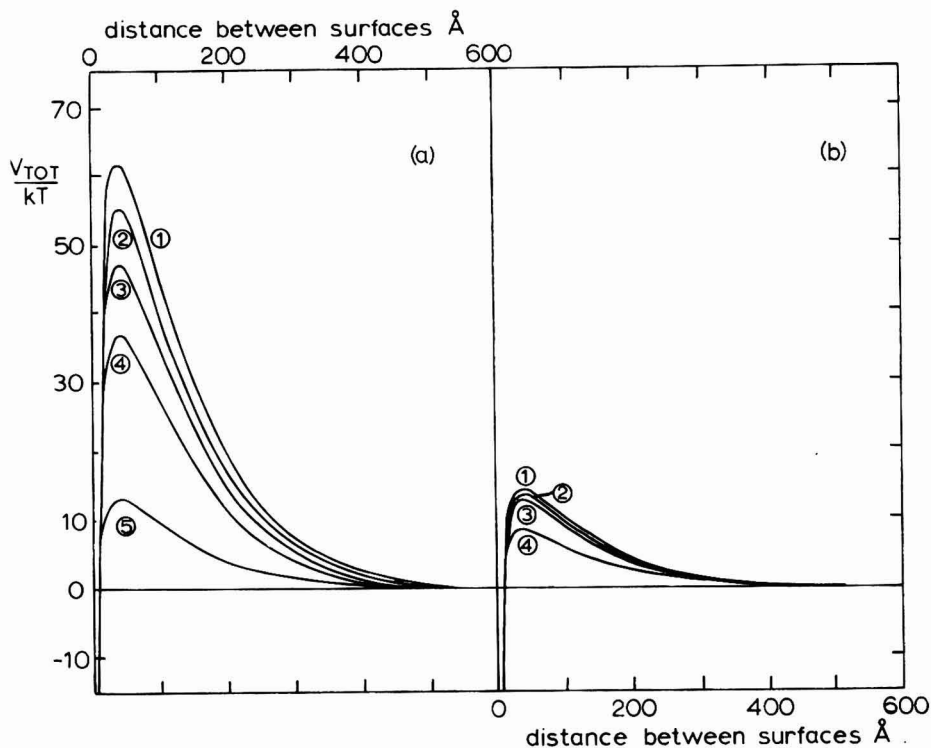


Fig. 11. The total potential energy as a function of the shortest distance between the surfaces of two spherical particles of similar surface potential ($\psi_0 = 35.86$ mV) and varying radius of one particle. $A = 5 \times 10^{-13}$ erg, $\kappa = 10^6$ cm $^{-1}$, $\epsilon = 78.5$

(a) $a_1 = 1250$ Å, $a_2 = 1250$ Å (1), 1000 Å (2), 750 Å (3), 500 Å (4), 125 Å (5)

(b) $a_1 = 125$ Å, $a_2 = 1250$ Å (1), 1000 Å (2), 750 Å (3), 125 Å (4)

Both are very relevant to an analysis of the stability of mixed pigment systems and of such phenomena as flooding and flotation. Dr. Wood, the present OCCA Fellow at the University of Nottingham, is working on the theoretical aspects of "heterocoagulation" in non-aqueous media, on which a report will be published later. Other than qualitative observations of flocculation behaviour in practical systems, there is no information to compare with the theoretical predictions. Certainly, no fundamental study has yet been carried out (to the author's knowledge), but the difficulties associated with such work must not be underestimated.

One further problem with applying theory to practice is the particle concentration effect. It is natural to raise the question of the application of the theory to systems that are so concentrated in pigment that the particle-particle interaction does not begin at "infinite" distance of separation, i.e. one particle is, on average, sufficiently close to another to reduce the effective energy barrier which must be overcome if contact is to be made. A preliminary theoretical attempt to solve this problem has been made³¹, but quantitative experimental results are not yet available for a worthwhile comparison to be attempted. Again, many parameters make the experiment rather difficult.

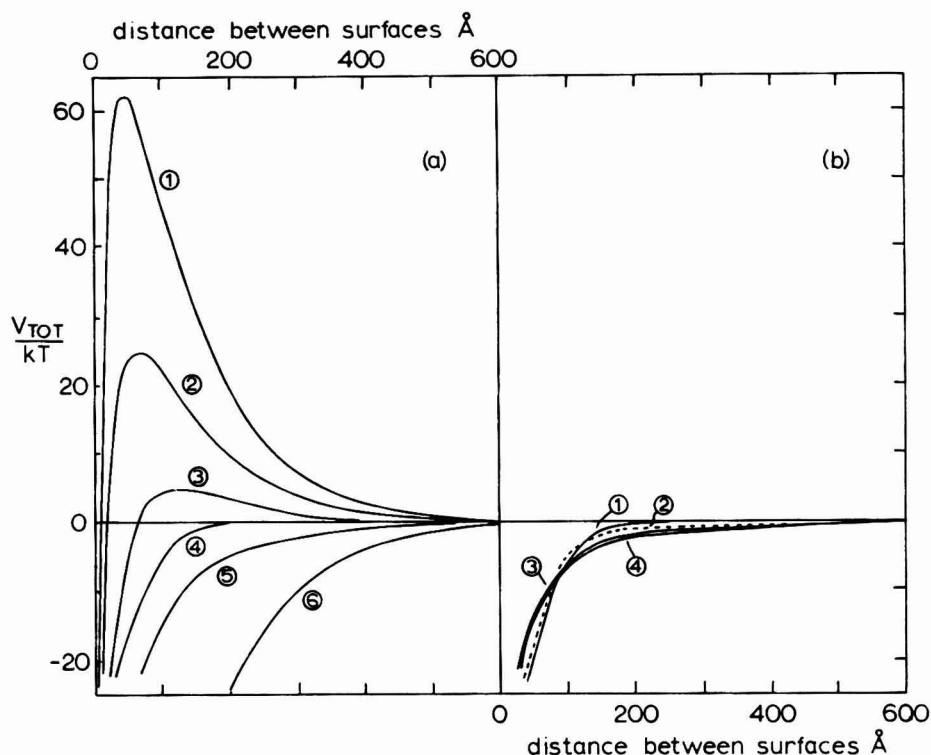


Fig. 12. The total potential energy as a function of the shortest distance between the surfaces of two spherical particles of similar radius ($a_1 = a_2 = 1250 \text{ \AA}$) and varying surface potential of one particle. $A = 5 \times 10^{-13} \text{ erg}$, $\kappa = 10^6 \text{ cm}^{-1}$, $\epsilon = 78.5$

(a) $\psi_{01} = + 35.86 \text{ mV}$, $\psi_{02} = + 35.86 \text{ mV}$ (1), $+ 20.48 \text{ mV}$ (2), $+ 10.24 \text{ mV}$ (3), $+ 5.12 \text{ mV}$ (4), 0 mV (5), $- 35.86 \text{ mV}$ (6)

(b) $\psi_{01} = + 5.12 \text{ mV}$, $\psi_{02} = + 35.86 \text{ mV}$ (1), $+ 20.48 \text{ mV}$ (2), $+ 10.24 \text{ mV}$ (3), $+ 5.12 \text{ mV}$ (4)

Repulsion due to steric and entropic effects

The stabilising effect associated with an adsorbed layer of non-ionic polymer molecules on the surface of pigment particles is well known in practical systems, although the mechanism is not clearly established. This type of stabilisation is less amenable to mathematical treatment than that in which double layers are concerned.

The effect of an adsorbed layer on the interaction between particles is related to the nature and thickness of the layer, and hence to the amount adsorbed. At low coverages, there is the possibility that parts of the adsorbed molecules become attached to two or more particles, bringing about flocculation by a "bridging" mechanism³². This is only possible when the surface coverage is low and parts of the surface are available for further adsorption, which may lead to bridging when the particles come into close proximity.

Essentially, there are two factors which must be considered to explain the stability of these uncharged systems. The first concerns the effect of the adsorbed layer on the attractive forces between particles. Vold³³ has shown theoretically

that, with the appropriate choice of surface active material, a significant reduction in the magnitude of the attractive force is possible. The distance between the surfaces of the particles when they collide is increased by twice the thickness of the adsorbed layer. Therefore, if no desorption occurs and the adsorbed layer is compact, and negligible attraction occurs between the material of the adsorbed layers, the stability will depend on the value of V_A corresponding to this distance and how it compares with the thermal energy of the particles³³. Calculations of this effect have been made²⁸ using the Vold equation for systems containing particles of pigmentary size with adsorbed layers of dimensions one might expect for such polymers as alkyd resins. In general, the attractive energy is reduced by the presence of an adsorbed layer, and the effect increases with increasing thickness of the adsorbed layer. Furthermore, the larger the particles the greater the thickness required to produce the same effect. Application of such an idea to a practical system might involve some estimation of adsorbed layer thickness, since this is not readily measured with any precision. Nevertheless it is well worthwhile.

The second factor arises when the situation is such that the attractive force between particles separated by twice the thickness of the adsorbed layer is still large, i.e. greater than at least ten times the thermal energy of the particles. Interpenetration of the adsorbed layers may then occur, particularly for smaller surface coverages of adsorbed molecules. The result is a decrease in entropy of the system (decrease in the number of possible configurations of the adsorbed molecules) and a corresponding reduction in the free energy of interaction. This constitutes a repulsive force, the magnitude of which may be sufficient to provide an energy barrier to flocculation. The effect of entropic repulsion has been treated theoretically for plane, parallel surfaces by Mackor and van der Waals³⁴, assuming the adsorbed molecules to be rigid rods anchored at one end to the surface by a freely hinged joint. More recently, Clayfield and Lumb³⁵ have considered the case of random polymer chains terminally adsorbed on plane surfaces and on spherical particles, and predict that the greater the freedom of movement of the polymer chain the more effective it is as a stabilising agent, provided that it remains adsorbed during the interaction between particles. Furthermore, the theory shows that there is an optimum size of molecule which will prevent adhesion of particles of a given size, and that increasing the length of the polymer chain may, in fact, increase the possibility of flocculation, which seems contrary to the effect described above. The reader is referred to the original paper for more detail. Unfortunately the amount of detailed experimental data available on this subject is very limited.

We have defined the principles of dispersion. Many parameters are involved in the dispersion process, and in practice they are often difficult to define explicitly. The value of fundamental work is obvious, but the significance of the results is not always appreciated, so that the preparation of a dispersion with the appropriate desirable characteristics is so often a matter of trial and error (with some inspiration). We have at our disposal some guiding principles which should, if wisely used, lead to better dispersion and to a better understanding of dispersion.

Acknowledgment

The work presented in Figs. 5 and 6 was carried out by Mr. D. G. Wharton and Dr. N. H. Picton; the computations shown in Fig. 10 were made by Dr. D. N. L. McGown and those in Figs. 11 and 12 by Dr. J. A. Wood. The assistance of these my colleagues is gratefully acknowledged.

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Discussion at the Scarborough Conference

DR. E. SUNDERLAND commented on the question of nomenclature. He felt Dr. Parfitt had been a little muddled on nomenclature in his lecture and that the matter had been rather over-complicated. Professor Nylén and himself had had very serious discussion on this and had come to the conclusion that only three types of definition were necessary.

First, there was the primary particle, which consisted of a number of crystallites and was not normally broken down during dispersing processes.

Secondly, the term "agglomerate" was chosen for an assembly of primary particles, which was generally broken down under normal dispersion conditions. The word "agglomerate" had been chosen in preference to "aggregate" because in most continental languages "aggregate" had other specialised meanings, and no intrinsic difference between the type of association which had been taken as "agglomerate" and as "aggregate" here could be seen.

The difference between a series of point contacts and surface contacts was not intrinsic; it was simply a quantitative difference and it was possible to have a whole range of surfaces in contact or a proportion of surfaces in contact; there was no real intrinsic difference.

A flocculate was simply defined as an assembly of particles which have come together from the wetted state.

It was felt that this covered all possibilities, simplified terms to three, and left possible all kinds of description which might be necessary in this field.

DR. PARFITT replied that he agreed entirely with the idea of reducing the number of terms, but unfortunately these seemed to have crept into the language. In his own abstract the term "aggregate" was used, but the term "agglomerate" was introduced in the lecture in keeping with a recent paper in *JOCCA*.

There was something to be said for differentiating between clusters of primary particles for which there was or was not an associated decrease in surface area. Furthermore, he was not convinced that the use of the single term "flocculate" was justified; the word suggested something loose. In practice there were many systems which, when they had "flocculated," did not form a loose sediment and were not easily redispersed; coagulated perhaps. A committee had been sitting recently on terminology in colloid science and had come to the conclusion that "flocculation" and "coagulation" should not be differentiated explicitly. It was important that each author clearly defined the terms he used.

DR. T. DOORGEEST commented that Dr. Parfitt had suggested that wetting was important in pigment dispersion, and that good stability was important, and agreed with these points. The problem of the breaking down of agglomerates and aggregates had not been mentioned.

In general it was thought that good wetting was identical with de-agglomeration of pigment agglomerates, or aggregates. He felt these were totally different. Good wetting was important and very helpful, but if the solvent or solution used penetrated all the cavities in the agglomerate, that would not necessarily mean that the agglomerate would fall apart into small agglomerates and primary particles. Would Dr. Parfitt discuss this point?

DR. PARFITT said that it was quite true that, although the internal surfaces of the aggregates were wetted, this did not mean to say they automatically fell apart. This was where the mechanical work was required. This had been seen, with certain commercial pigments, which, when brought into contact with a liquid, virtually exploded, provided they were wetted, and the energy required to produce a dispersion was minimal. In these cases, displacement of air led to sufficient energy to break down the aggregates. This seemed to be the ideal case. Many factors determined the relative importance of the wetting and milling processes.

DR. DOORGEEST said that the stir-in pigments should be excluded, as they were manufactured by enveloping primary particles with a binder, and could not cement together during the drying process, so were totally different materials from those under discussion. The discussion was about agglomerates and aggregates as they

were present in normal pigments. There was a difference between a good wetting solvent and a bad wetting solvent, but that did not mean that agglomerates present in well dried pigments broke down into smaller fragments if they were wetted by a good wetting solvent or by a good wetting solution. Something else had to be done, that was breaking down the agglomerates, and therefore mechanical work was needed. He would like to stress that good wetting was important, but it was not the end of the story.

MR. R. R. DAVIDSON said that he would like to reinforce what Dr. Doorgeest had said. In his experience the only way to be quite clear in discussing the incorporation of powders into liquids was to use the term "cemented aggregate" when dealing with powders where the primary particles were cemented together. The term "cemented agglomerate" was possible, but it was the term "cemented" which was important. It meant that bonds existed between the primary particles either consisting of dried mother-liquor or being of a co-crystalline nature. If such bonds did not exist, dispersion of primary particles was in general very easy.

Obviously no amount of "wetting" action or of addition of surface active agents would break apart a particle which was like a dumb-bell with a solid cementing neck between two primary particles. Mechanical breaking of the neck was required.

Surface active agents could, of course, help by enabling the particles to be so packed together in a suspension of suitable flow properties that particle breakage by inter-particle attrition was greatly increased by a given milling procedure.

Further, there was the Reh binder effect. Reh binder showed that surface active agents could have a pronounced effect in accelerating the breaking down of cemented aggregates or of large crystalline particles. Apparently the mechanism in ball milling was something like this. During the milling micro-cracks were formed. Surface active agents or solvents penetrated into these cracks and helped to open them by a kind of levering action. It was as though a wedge were being driven into the crack.

He asked if Dr. Parfitt would care to say something about the Reh binder effect.

DR. PARFITT replied that the question one must ask was whether the cracks existed *before* milling; evidence existed from "t" plots of cracks existing on a rutile surface. If these were annealed out then the effect of the surface active agent might not be as relevant. As far as he knew there had been no study of this effect, but he felt that annealing of cracks on oxide surfaces and the effect on the milling process and on the energy required to mill could give some information on the Reh binder effect.

MR. SCHAEFFER referred to work by Mr. Cozzens several years ago at Lehigh University, in which a combination of devices, which were very pertinent to the points that had been made on this question of the energy involved in de-agglomeration and de-aggregation of pigments, were used. Mr. Cozzens used a Band Viscometer, which was an instrument originally devised by Asbach and co-workers in Germany, and was effectively a kinetic type of viscometer in which there was a rectangular orifice, the thickness of which was defined by shims; there was a water-cooled system and a small reservoir in the top, with a means of tightening this to a required thickness. A hand mixed dispersion, or rather a very poorly pre-mixed system of aggregate at a concentration—less than 1 per cent—was examined, where the particle-particle interaction in the dispersion process would be expected to be negligible, if not nil. The band was then loaded with a given mass, and allowed to pull a tape—in this case a Mylar tape—through the orifice, pulling the fluid, the dispersion, through with it. On the basis of the time of exposure of the dispersion in the band and the known mass, one had effectively a viscometer, and one could also compute the total energy that was put into this dispersed system. The order of magnitude used in this system was 1 to 10 joules, and carbon black dispersed in polybutenes and various types of litho varnishes was examined, after passing through the viscometer and being

diluted to concentrations of the order of 1/1,000th to a 1/10,000th per cent of carbon black, and the optical transmission was measured in much the same way as Dr. Parfitt had done. If the per cent transmission was plotted as a function of the energy input for an entire range from double zero litho varnish to No. 4 litho varnish with one carbon black, a linear relationship was obtained, of fairly broad band, but precise enough for this type of work with dilution and all that was involved, relating the decrease in per cent transmission total energy input to the system in a linear fashion.

If polybutene was introduced into this system, instead of the litho varnishes, much more of a dispersion was obtained in a poorer wetting system, but in effect the slopes of the curves remained the same, which meant that the efficiency with which de-aggregation was occurring with a known amount of energy put into the system was approximately comparable. The difference was the initial states of the dispersions. There was no way of hand mixing a pigment into a vehicle under very low shear in such a way as to avoid this difference in surface chemistry in the initial contacting of the vehicle with the pigment.

The next step was to introduce into both of these systems a lecithin as a wetting agent, to improve the behaviour of the polybutene and the litho varnishes. In both these cases exactly the same effect occurred. The initial curves for the initial lecithin were parallel, so the same efficiency was being obtained, with one exception. When the temperature of one litho varnish, a No. 3 litho varnish, was increased from 25 to 35 and 45° C in the viscometer, then the slope of the curve changed; so that apparently at the higher temperature limits an increased efficiency in the utilisation of the available energy in the viscometer was being obtained.

Communicated addition

DR. J. A. W. VAN LAAR observed that an interesting practical case of the various connections between the contact angle θ and the wetting was the behaviour of aluminium pigment. This occurred in flakes and during making was treated at the surface by what was assumed to be stearic acid. Usually these pigments were stirred easily into the vehicle, an oil or a resin, diluted with one or more solvents. This then would mean that the contact angle was between 90° and zero.

During the evaporation of the solvents the surface tension at the liquid/air interface increased, thus causing the well-known circulations in the drying film. This circulation brought the aluminium flakes to the surface. With certain kinds of aluminium the so-called "leafing" then took place. The aluminium remained at the surface. Evidently the contact angle was now over 90°. The reason might be part evaporation of the solvent, the interface liquid/air thus having been changed. "Leafing" power might disappear with time.

Other aluminium pigments remained in the liquid (metallic effect and hammer-tone finishes) and apparently the contact angle had not decreased here.

The remark was made, firstly, to ask Dr. Parfitt for a possible comment or explanation, and secondly, to show appreciation for and give an illustration to his theoretical survey and bridge the gap between theory and practice.

DR. PARFITT replied that he was unfamiliar with "leafing" behaviour and therefore hesitated to put forward an explanation. What Dr. van Laar had said seemed very reasonable, but what was the basic difference in the surfaces of the various aluminium pigments that might lead to differences in wetting behaviour?

The adsorption of long chain acids on to rutile from n-heptane

By R. H. Ottewill and J. M. Tiffany*

School of Chemistry, University of Bristol, Bristol 8

Summary

The adsorption of stearic, oleic, linoleic and linolenic acids on to rutile from n-heptane has been measured at temperatures of 5°C and 25°C, using dried materials. All the materials used were carefully characterised. Radiotracer methods using C¹⁴ labelled acids were employed to estimate the extent of adsorption at low equilibrium concentrations of adsorbate. With stearic acid a vertically oriented monolayer was obtained. With all the unsaturated acids stepped isotherms were obtained and these have been interpreted in terms of reorientation of the molecules on the rutile surface. Multilayer adsorption appeared to occur at high concentrations of unsaturated acids.

L'adsorption par rutile des acides en chaîne longue à partir des solutions dans n-heptane

Résumé

On a déterminé, à l'aide des matériaux pré-séchés, l'adsorption par rutile des acides stéarique, oléique, linoléique et linoléique à partir des solutions dans n-heptane à des températures de 5°C et 25°C. Tous les composés utilisés dans cette investigation ont été rigoureusement caractérisés au point de vue de leur composition chimique. Des méthodes de traçage radioactif avec le C¹⁴ ont été utilisées pour faire le dosage de l'adsorption à de faibles concentrations d'équilibre de l'adsorbat. Dans le cas de l'acide stéarique on obtenait une monocouche orientée verticalement. Dans le cas de tous les acides non-saturés on obtenait des isothermes en gradins que l'on a interprétées en termes de la réorientation des molécules sur la surface du rutile. L'adsorption en multicouche paraissait à se présenter aux concentrations élevées d'acides insaturés.

Die Adsorption Langkettiger in n-Heptan Gelöster Säuren auf Rutil

Zusammenfassung

Die Adsorption auf Rutil von in n-Heptan gelösten Stearin-, Olein-, Linol- und Linolensäuren wurde bei 5 und 25°C gemessen, wofür getrocknete Prüfmuster verwendet wurden. Alle Stoffe wurden sorgfältig gekennzeichnet. Um den Adsorptionsgrad bei niedrigen Gleichgewichtskonzentrationen des Adsorbates zu bestimmen, wurden Radioindikatormethoden unter Verwendung von mit C¹⁴ markierten Säuren benutzt. Mit Stearinsäure wurde eine vertikal orientierte, monomolekulare Schicht erhalten. Mit allen ungesättigten Säuren wurden abgestufte Isothermen gefunden, die im Sinne von molekularer Neuorientierung auf der Rutiloberfläche interpretiert wurden. Bei hohen Konzentrationen ungesättigter Säuren erfolgte scheinbar Adsorption in mehreren Lagen.

Адсорбция длинно-цепочных кислот на рутиле из n-гептана

Резюме

Адсорбция стеариновой, олеиновой, линолеиновой и линоленовой кислот на рутиле из n-гептана измерялась при температурах в 5°C и 25°C, применяя сухие материалы. Все применяемые материалы были тщательно охарактеризованы.

*Present address: Department of Microbiology, University of Pennsylvania, Philadelphia 4, Pa., USA.

Радиоактивно-индикаторные методы с кислотами мечеными C^{14} применялись для оценки степени адсорбции при низких равновесных концентрациях адсорбата. В случае стеариновой кислоты был получен вертикально ориентированный монослой. В случае всех ненасыщенных кислот были получены ступенчатые изотермы, которые объяснялись переориентацией молекул на поверхности рутила. Многослойная адсорбция повидимому имела место при высоких концентрациях ненасыщенных кислот.

Introduction

Although a large amount of literature is available on the adsorption of various materials from solution on to solid surfaces¹, very few precise measurements appear to have been carried out on the adsorption of unsaturated fatty acids on to rutile and there is a lack of precise information on the adsorption of such molecules in the low concentration region. Unsaturated acids are notable as compounds which can confer stability on dispersions in non-aqueous media² and it is therefore of some importance that their mode of adsorption should be understood in some detail. The aim of the present work was to examine under well-defined conditions the adsorption of a series of acids of constant chain length on to rutile from n-heptane. The series commenced with the fully saturated acid, stearic, and included the following unsaturated acids :

oleic (cis-form) $C_8H_{17}CH=CH(CH_2)_7COOH$

linoleic (cis-form) $C_{18}H_{33}CH=CHCH_2CH=CH(CH_2)_7COOH$

linolenic (cis-form) $C_{19}H_{35}CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_4COOH$

The adsorption measurements were carried out using C^{14} labelled acids as tracers and adsorption isotherms were obtained at temperatures of 5°C and 25°C. It was thus possible to carry out some thermodynamic analysis on the results obtained.

Experimental

Materials

n-Heptane : The n-heptane, which was Hopkin and Williams material, was dried by slowly running through a 1.5-metre-long column packed with beads of Union Carbide molecular sieve-4A. The latter was freed from water before use by heating in vacuo at 150°C for 24 hours. After drying, the n-heptane was distilled and the fraction which boiled between 98.40 and 98.45°C at 760 mm collected. A small amount of rigorously dried rutile was added as a "getter" to remove the remaining traces of water and the material stored in glass stoppered flasks in a dry box. The water content of the n-heptane so treated was less than 0.01 mg per ml.

The refractive index, n_D^{20} , was found to be 1.3881 compared to the literature value³ of 1.38764.

Titanium Dioxide : This was a rutile sample kindly prepared by British Titan Products Company Limited in their laboratories, by hydrolysis of titanium tetrachloride. The material as supplied had been heated at 420°C for three hours, and X-ray analysis showed that the anatase content was approximately 2 per cent.

A thin slurry of rutile was prepared and adjusted to a pH in the range 9-11 to obtain a reasonable dispersion. The slurry was introduced into Viskase

dialysis sacs and dialysed against double distilled water with constant stirring of the dialysate and frequent changes of water. After about a week there was no difference in conductance of the water used before and after dialysis. The rutile was therefore separated by centrifugation and heated in a vacuum system (10^{-4} mm Hg) at about 400°C for 24 hours. Carefully dried air was admitted after cooling and the rutile was subsequently stored in a dry box. The dry box was supplied with nitrogen gas obtained by boiling liquid nitrogen and the pressure inside the box was maintained at a pressure greater than atmospheric. The water content of nitrogen prepared in this way is 10^{-23} mg/litre of gas at normal temperature and pressure.⁴

The zero point of charge of the material was found to occur at $\text{pH}=4.62$ as determined by microelectrophoresis in 10^{-3} M sodium chloride solution.

A thermogravimetric analysis of dried but unheated rutile showed two main peaks, one in the range $300\text{-}400^{\circ}\text{C}$ and the other in the range $650\text{-}750^{\circ}\text{C}$.

The surface area of the sample was determined by the BET method using krypton adsorption at liquid nitrogen temperatures. A value of 14.2 ± 1 m^2/g was obtained which corresponds to a mean spherical diameter per particle of 0.097μ .

A mass spectrographic analysis of the material gave the following results :*

<i>Element or Oxide</i>	<i>Amount found (p.p.m.)</i>
Cl	50
Al_2O_3	50
P_2O_5	30
K_2O	25
CaO	9
V_2O_5	<0.02
Cr_2O_3	<0.02
Fe	5
MnO	0.01 .
As_2O_3	0.5
Sn	2.5
Pb	0.6
SiO_2	100

Except for the presence of silica and some chloride the trace element content of the material was small.

Inactive Fatty Acids : Stearic, oleic, linoleic and linolenic acids were all obtained from Fluka Chemicals as Purissimum grade materials : in all cases the acid was stated to be not less than 99.5 per cent *cis* acid. All the acids used were quite clear and completely colourless and each ampoule was used immediately after opening in a dry box. Solutions of the acids in n-heptane were also stored in a dry box.

The refractive indices of all the liquid acids were measured at 20°C using a Pulfrich refractometer and compared with literature values. The results are recorded in Table 1.

*Our thanks are due to Messrs. British Titan Products Company Limited for carrying out this analysis.

Table 1
Refractive indices of unsaturated acids, n_D^{20}

Acid	n_D^{20} found	n_D^{20} literature	Reference
Oleic	1.4577	1.4582	5
Linoleic	1.4720	1.4710	6
Linolenic	1.4785	1.4795	7

The melting point of the stearic acid was found to be 69.5°C compared with the literature value⁸ of 69.6-69.8°C. Determination of a surface pressure against area curve on a Langmuir trough gave two sharply defined straight sections which on extrapolation to zero surface pressure gave areas per molecule of 20.6 and 25.2 Å² in good agreement with literature values^{9, 10}. The solubility of stearic acid in n-heptane at 5°C was found to be 1.77×10^{-3} and at 25°C a value of 1.39×10^{-2} M was obtained.

Radioactive Acids : All the acids were obtained as C¹⁴ labelled materials from the Radiochemical Centre, Amersham. In view of the small quantities of radioactive acids which were used, ca. 1.25 mg, no attempt was made to purify these materials further and they were used as obtained. The precision of the adsorption measurements is affected by the purity of these acids and the indistinctness of the adsorption isotherms for linolenic acid could be due to the relatively large amounts of *trans* acid present in this material.

The acids as supplied were in solution in benzene in sealed Pyrex ampoules. The ampoules were opened in a dry box and the benzene allowed to evaporate in a gentle stream of dry nitrogen. The acid was then dissolved in dry n-heptane, transferred to a graduated flask and made up to 100 ml. A series of stock tracer solutions were prepared and stored in the dry box. The details of the labelled acids used are recorded in Table 2.

Table 2
Details of radioactive acids

Acid	Specific activity mC/mM	Radiochemical purity	Chemical purity
Stearic	34.6	99%	—
Oleic	24.6	99%	<i>trans</i> content 3% acid content 99%
Linoleic	24.7	91%	<i>trans</i> content 8% acid content 99%
Linolenic	22.0	89%	<i>trans</i> content 15% acid content 99%

Determination of adsorption isotherms

Adsorption experiments were carried out using graduated conical-ended 10 ml centrifuge tubes fitted with B 14 ground glass stoppers. The stoppers were fitted with Teflon sleeves to reduce the creep of the heptane through the joints. The initial solutions of fatty acid were made up in the tubes in a dry box and

the tubes were then agitated in an end-over-end shaker in an air thermostat whose temperature could be controlled to within 0.1°C . After a few hours, when the solution had come to adsorption equilibrium with the glass, a two ml sample was withdrawn for counting. In this way an adsorption isotherm was constructed for the glass tubes over the range of concentrations to be investigated. It was found that the adsorption on the glass could conveniently be fitted by a Freundlich isotherm and be used in this form for correcting the final results.

A weighed amount of dry rutile was added to each tube and the tubes were returned to the air-thermostat and shaken until equilibrium had been established. This required ca. 15 hours at 25°C and ca. 40 hours at 5°C . The tubes were then centrifuged until a clear supernatant liquor was obtained, the final volume of solution noted, and a further 2 ml of solution removed for counting. The centrifuge was housed in the air thermostat so that the tubes were not subjected to sudden changes of temperature which might have affected the adsorption equilibrium. The high density of the rutile enabled effective separation to be obtained at relatively low speeds, so that little heat was generated in the thermostat box by the centrifuge motor.

The 2 ml aliquots removed for counting were immediately added to 5 ml of a toluene solution of scintillator in the counting vials. The vials were stoppered and stored in the dark until required for counting. Counting was carried out using an Ekco N 664 B liquid scintillation counter in conjunction with an Ekco N 610 A scaler unit.

If the counting rate of the initial sample is taken as R_I , that of the liquid in equilibrium with the solid as R_F and the concentration of the initial solution is c_I moles/litre, after allowing for the adsorption on the glass, then the final concentration is given by,

$$c_F = c_I (R_F/R_I) \text{ moles/litre.}$$

The acid adsorbed on the walls of the glass tubes did not appear to desorb during the period of equilibration with rutile and, since the amount concerned was small, it was assumed that the acid adsorbed on the walls played no further part in the adsorption process. Thus, taking the volume of solution as V and the amount of solid as m grams, then the moles adsorbed per gram is given by,

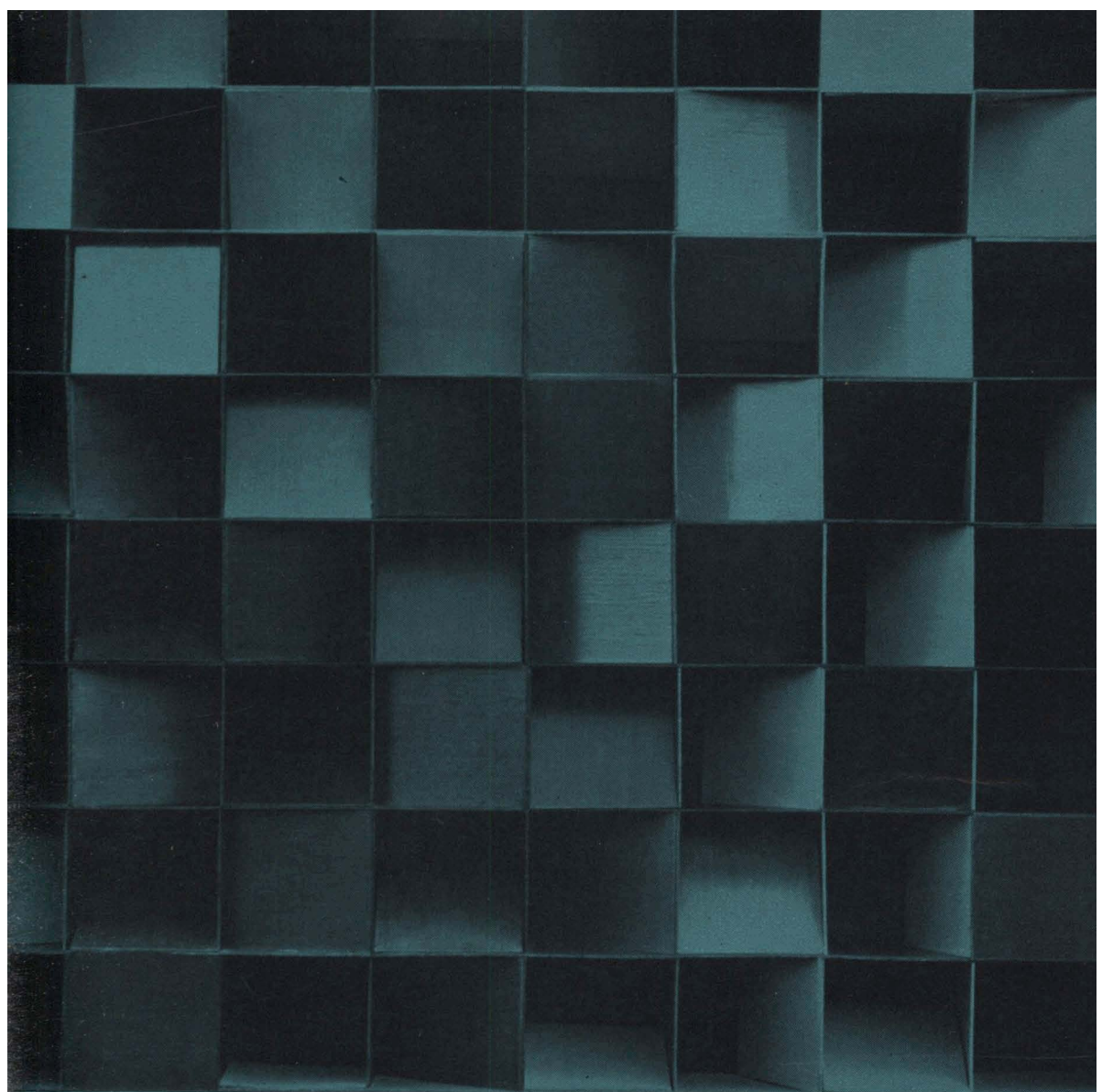
$$c_I (R_I - R_F)V/1000 m R_I$$

Variation of the mass of solid to the volume of solution did not affect the results obtained, so that, in general, 0.1 gram of rutile was employed, unless this brought about too large or too small a change in concentration for convenient counting.

Results

(i) Adsorption isotherms

It is known that fatty acids are often dimerised to some extent in organic solvents, owing to hydrogen bonding between the carboxyl groups, and an attempt was made to determine the extent of dimerisation of the acids in solu-



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tion using infra-red spectroscopy¹¹. Although the peaks arising from the monomeric and dimeric forms could be resolved and it was clear that the monomer-dimer equilibrium was markedly concentration dependent, only qualitative estimates of the equilibrium constant were found possible. For this reason all the adsorption isotherms have been reported as, n_1 , moles of adsorbed acid per gram of solid, against the equilibrium concentration of monomeric acid, c , expressed as moles/litre.

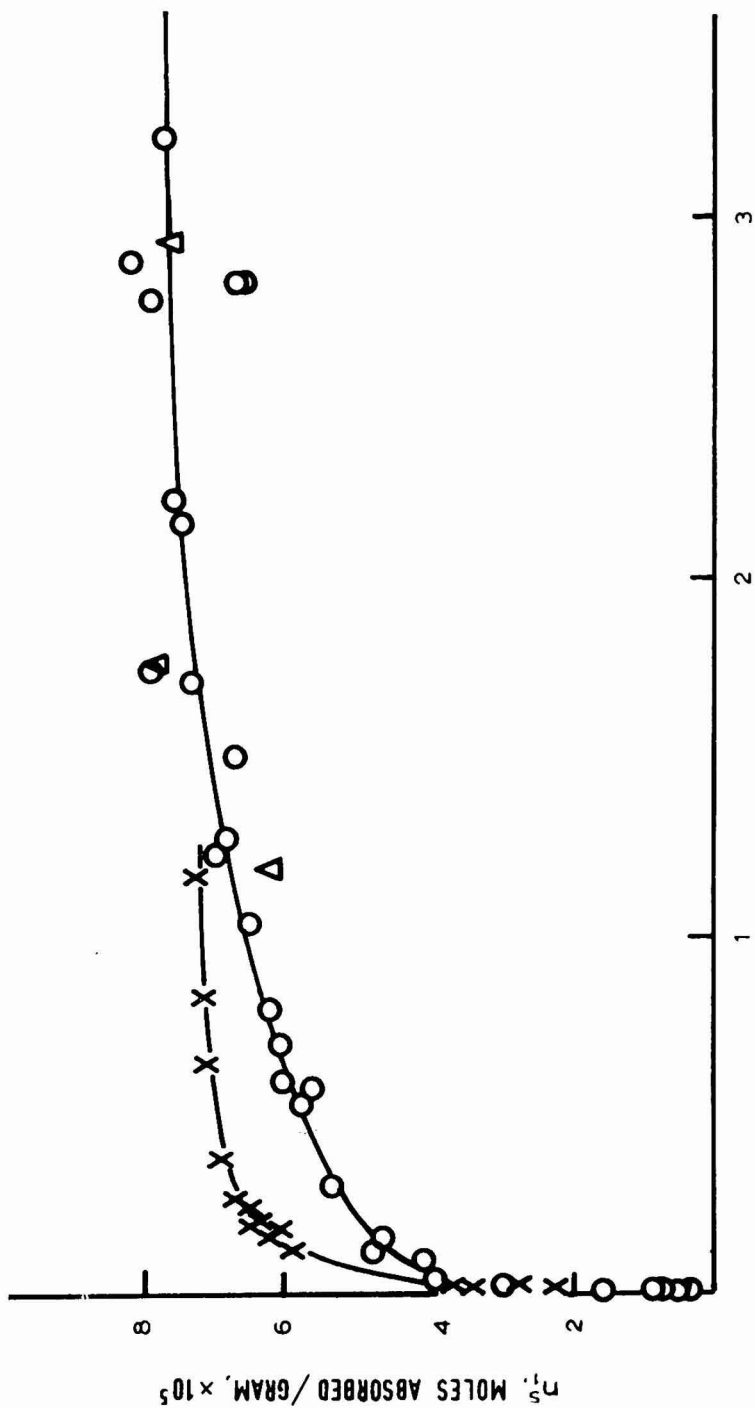
An interesting feature of the adsorption work was that all the isotherms showed less scatter at low, than at high concentrations. This may well be connected with the greater percentage of monomer present at concentrations of 5×10^{-4} M or less, and the reduced necessity in this range for dissociation of the acid before adsorption of the monomer could take place.

Stearic acid: The adsorption isotherms obtained at 5°C and 25°C for the adsorption of stearic acid on to rutile are given in Fig. 1. The amount adsorbed increased rapidly at low concentrations and then reached a plateau region where the adsorption of the acid changed only by a small amount with increase in concentration of acid in the bulk phase. The maximum amounts adsorbed were 7.4×10^{-5} moles/g at 5°C and 8.15×10^{-5} moles/g at 25°C. The results obtained using radioactive acids at 25°C were checked against results obtained using the Langmuir trough as a means of obtaining the concentration of the adsorbed material. Good agreement was obtained between the results obtained by both methods (see Fig. 1).

Oleic acid: The adsorption isotherms obtained for oleic acid are given in Fig. 2. In contrast to the results obtained with stearic acid two steps were observed on the isotherm. The first step occurred at an amount adsorbed of 5×10^{-5} moles/gram at both 5°C and 25°C. The adsorption at 25°C increased rapidly after the first plateau region and did not reach a constant value within the range of equilibrium concentrations used in these experiments. However, it appeared to be tending to a limit at ca. 2.0×10^{-4} moles/gram. At 5°C a considerable amount of scatter was observed in the results in the region of the second step and the curve crossed the 25°C curve.

Linoleic acid: The adsorption isotherms obtained at 5°C and 25°C using linoleic acid are given in Fig. 3. Three distinct steps are apparent. At 5°C the plateau regions occurred at ca. 5.5×10^{-5} , 8.0×10^{-5} and 1.5×10^{-4} moles/gram and at 25°C at 4.2×10^{-5} , 7.9×10^{-5} and 1.3×10^{-4} moles/gram. The scatter in the points at the higher concentrations found with oleic acid was not observed with linoleic acid.

Linolenic acid: Studies on the adsorption of linolenic acid proved to be more difficult than with the other acids and more scatter was apparent on the adsorption isotherms. The latter are given in Fig. 4. A well defined step was observed at 25°C at an equilibrium concentration of 4.0×10^{-3} M. Some evidence of steps was apparent at the lower amounts adsorbed but these could not be resolved as clearly as with the other acids.



c, MOLAR EQUILIBRIUM CONCENTRATION $\times 10^3$

Fig. 1. n_1 against c for the adsorption of stearic acid on rutile from n-heptane, — x —, 5°C; — o —, 25°C. — Δ —, points obtained using a Langmuir trough for analysis of equilibrium solutions

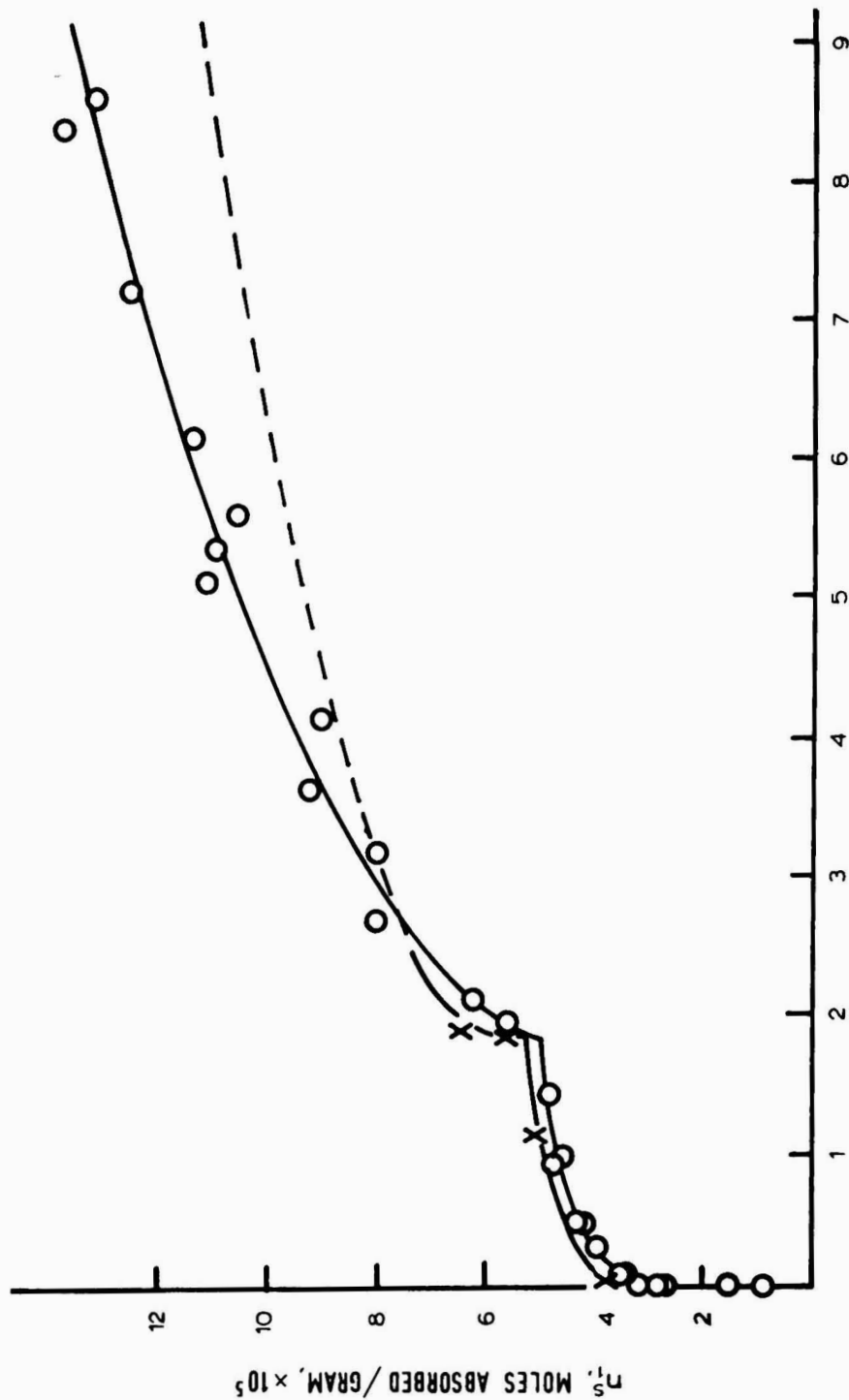


Fig. 2. n_s against c for the adsorption of oleic acid on rutile from n-heptane, — x —, 5°C; - - o - - mean curve from scattered results at 5°C.

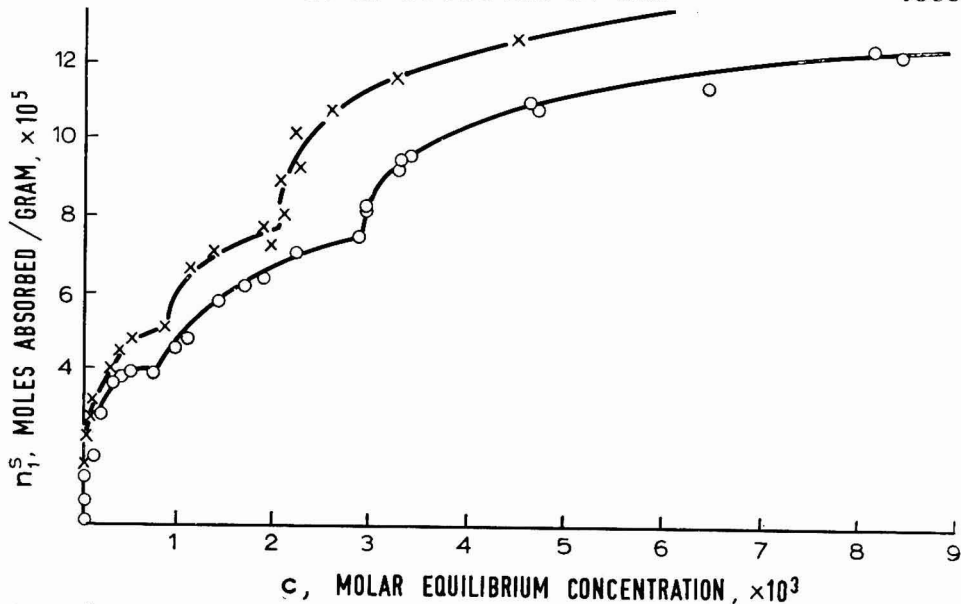


Fig. 3. n_1^s against c for the adsorption of linoleic acid on rutile from n-heptane, — x —, 5°C ; — o —, 25°C

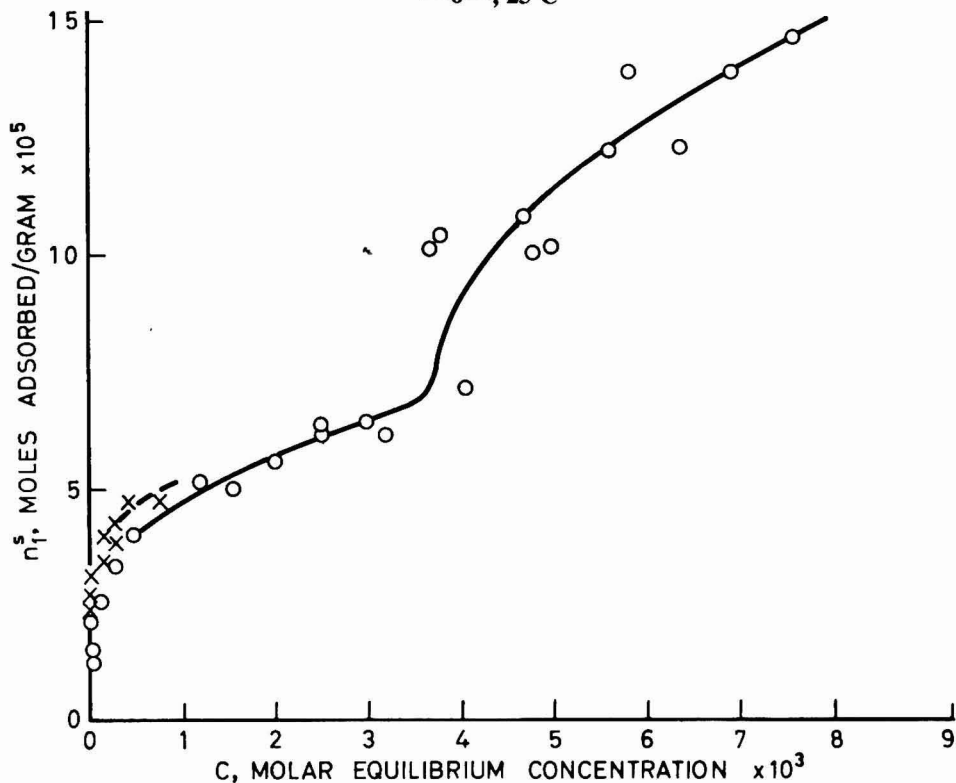


Fig. 4. n_1^s against c for the adsorption of linolenic acid on rutile from n-heptane, — x —, 5°C ; — o —, 25°C

(ii) *Geometrical considerations of the packing of unsaturated acids at interfaces*
 In order to assist with the interpretation of the adsorption isotherms, Catalin models were made of all the molecules used in the present work and their projected areas measured in various orientations. In the case of the unsaturated acids, the number of possible points of attachment to the surface can be found directly from the number of double bonds in the chain. Generally, for a molecule with n bonds, there are $(n + 1)$ possible points, since in cases where the main attachment is through the carboxyl group there are associated 0, 1, 2, — — — — n positions in which double bonds can come into contact with the surface. The results obtained are summarised in Table 3.

Table 3
Projected areas of Catalin models

Acid	Orientation	Area-A ² per molecule
Stearic	Horizontal	92.5
	Vertical	20.5
Oleic	Horizontal	90.5
	2-point attachment	48.0
Linoleic	Horizontal	87.5
	3-point attachment	62.0
Linolenic	Horizontal	85.5
	4-point attachment	74.0

An alternative approach was to consider the packing of molecules on to a rutile surface. In order to ascertain the extent of packing, paper models of the projected areas of the acids in various orientations were arranged on site distribution diagrams for rutile, prepared according to the distribution of the oxygen atoms on the predominant crystal faces of a rutile crystal. Electron microscope examinations showed that all the primary particles were acicular crystals of closely similar shape with an axial ratio of ca. 3:1. It seemed reasonable to assume that the predominant faces were $\{100\}$, $\{110\}$, $\{101\}$ and $\{111\}$, of which the latter contributed only a small amount to the total area. Thus, the faces $\{100\}$, $\{110\}$ and $\{101\}$ were taken to constitute respectively 25 per cent, 45 per cent and 30 per cent of the total area. The results obtained are given in Table 4. It can be observed from a comparison of Tables 3 and 4 that

Table 4
Area per adsorbed molecule on crystal faces in A²

Acid	Orientation	Area/molecule of face			Mean area/molecule
		(100)	(110)	(101)	
Stearic	Horizontal	85.3	115.9	112.5	107.2
	Vertical	27.3	26.8	25.1	26.4
Oleic	Horizontal	95.3	128.5	112.8	115.4
	2-point attachment	54.5	48.0	62.5	54.0
Linoleic	Horizontal	92.0	124.1	109.0	111.6
	2-point attachment	54.5	48.0	62.5	54.0
Linolenic	3-point	54.5	96.5	75.4	79.6
	Horizontal	90.1	121.6	106.7	109.1
	4-point	81.7	115.6	125.5	110.0

the area per molecule is much larger in many cases than that obtained by projection of the Catalin models. This is because there is, in all cases, space between the adsorbed molecules which cannot be filled, owing to the restriction of access either to the surface generally or to specific sites, by either an acid or a heptane molecule.

Discussion

(i) *The adsorption isotherms*

The maximum adsorption of stearic acid at 25°C was found to be 8.15×10^{-5} moles/gram. On the basis of a surface area of 14.2 m²/gram this corresponds to an area per adsorbed molecule of 29 Å². If, however, 20.9 Å² is taken for the close packed area of stearic acid, the maximum extent of adsorption corresponds to 71 per cent of a vertically oriented monolayer. This is in close agreement with the work of Kipling and Wright¹², who found for the adsorption of stearic acid on anatase from cyclohexane that in the region of maximum adsorption 68 per cent of the surface was covered by a vertically oriented monolayer. From geometrical considerations of the closest packing of saturated fatty acid molecules on the various idealised crystal planes of rutile, the figures shown in Table 4 correspond to an area of 26.4 Å². The maximum adsorption observed on this basis would correspond to 91 per cent of a monolayer. Within the limitations imposed by the use of the BET method to determine the surface area of the rutile sample, it would appear reasonable to conclude that stearic acid forms a vertically oriented monolayer on rutile on adsorption from n-heptane under dry conditions.

The adsorption isotherms for oleic acid exhibit two steps; some difficulties were experienced in determining the isotherm at the high concentrations of oleic acid and for this reason the curve is shown as a dotted line in this region in Figure 2. The first step which occurs at 5.0×10^{-5} moles/gram at both temperatures corresponds to an area per molecule of 47 Å², a value close to the 54 Å² obtained from molecular models on the basis of a two-point attachment of the molecule to the surface (see Table 4). The second step on the isotherm at 25°C did not level out. The extent of adsorption continued to increase, indicating the formation of multilayers. However, a slight shoulder did occur at 9×10^{-5} moles per gram. This corresponds to an area per molecule of 26 Å² and might infer the completion of a vertically oriented monolayer before the onset of multilayer formation.

In the case of linoleic acid, the isotherms exhibited steps at 25°C at 4.2×10^{-5} (56 Å²), 7.9×10^{-5} (30 Å²) and 1.3×10^{-4} moles/gram (18 Å²). The first step appears to be in agreement with a 2-point attachment, and the second with approximately the area expected for completion of a perpendicularly oriented monolayer. Again, however, as in the case of oleic acid at 25°C the curve did not appear to reach a saturation value indicating that some multilayer formation was occurring.

The isotherm for linolenic acid showed a well defined step at 6.5×10^{-5} moles/gram at 25°C corresponding to an area per molecule of 36 Å². There is, however, some uncertainty in the points in this region and the area per molecule could be considerably lower, i.e. close to that expected for a vertically oriented layer of linolenic acid. The low concentration end of the isotherm also indicates

the presence of two steps, one at 2.9×10^{-5} moles/gram (81 \AA^2) and one at 3.6×10^{-5} moles/gram (66 \AA^2). These areas per molecule are close to those expected for 3-point and 2-point attachment of the molecules respectively. A saturation value for the adsorption was not observed with this material at the highest concentrations examined, and from the extent of adsorption it is clear that multilayer adsorption occurs.

In the recent work of Sokola *et al.*¹³ the adsorption of linoleic acid on to rutile of various moisture contents was examined from toluene solution. On moist rutile a Langmuirian isotherm was obtained, but on "dry" rutile a two stepped isotherm was observed. These authors apparently found a saturation value for the second step and attributed this to the formation of a bimolecular layer of linoleic acid, although the amount adsorbed was in excess of that required for a bimolecular layer.

The present results suggest that, in the adsorption of unsaturated acids, the molecule first resides on the surface, with the carboxyl group and the double bonds as the points of contact. The molecule then gradually stands up with increasing concentration until a vertical orientation is assumed. The single layer of vertically oriented molecules appears to be followed by multilayer formation with all the unsaturated acids examined in the present work. The formation of such thick layers probably accounts for the fact that unsaturated acids often confer considerable stability on dispersions in non-aqueous media.²

The mechanism proposed is supported by the recent work of Sherwood and Rybicka¹⁴. In the case of the adsorption of oleic acid on titanium dioxide pigments, these authors found considerable perturbation of the double-bond stretching frequency in the infrared spectrum of the adsorbed acid. On material adsorbed from solutions of low concentration, the band at 3007 cm^{-1} was entirely absent. Material prepared from solutions of higher concentration showed a weak band which was shifted to a higher frequency. The $-\text{CH}_2-$ frequencies in oleic acid were also perturbed, in the presence of the surface, from their positions in the spectrum of the pure liquid or a solution of the acid. This result was taken to infer some interaction of the hydrocarbon chain of the acid with the surface, as might occur in a completely horizontal or two-point attachment. Some evidence was also found for the formation of multilayers in the case of oleic acid.

(iii) Thermodynamic analysis

The adsorption isotherms obtained for stearic acid indicate that monolayer formation occurs with this compound. Some attempt has therefore been made to obtain thermodynamic information from the data obtained. The Langmuir adsorption isotherm, following Everett¹⁵, can be written for dilute solutions in the following form,

$$c/n_1^* = 1/Kk_1.N_s + (K-1).c/K.N_s$$

where K = a surface equilibrium constant, $k_1 = 1/6.8$, a factor introduced to convert equilibrium concentrations of acid into mole fractions, and N_s = moles of acid/gram required to form a close packed vertically oriented layer.

The data for stearic acid at 5°C and 25°C are plotted in Fig. 5 as curves of c/n_1^* against c . Over the range of n_1^* values from 4.7×10^{-5} to 7.3×10^{-3} moles/gram, reasonably linear plots were obtained and the adsorption appeared

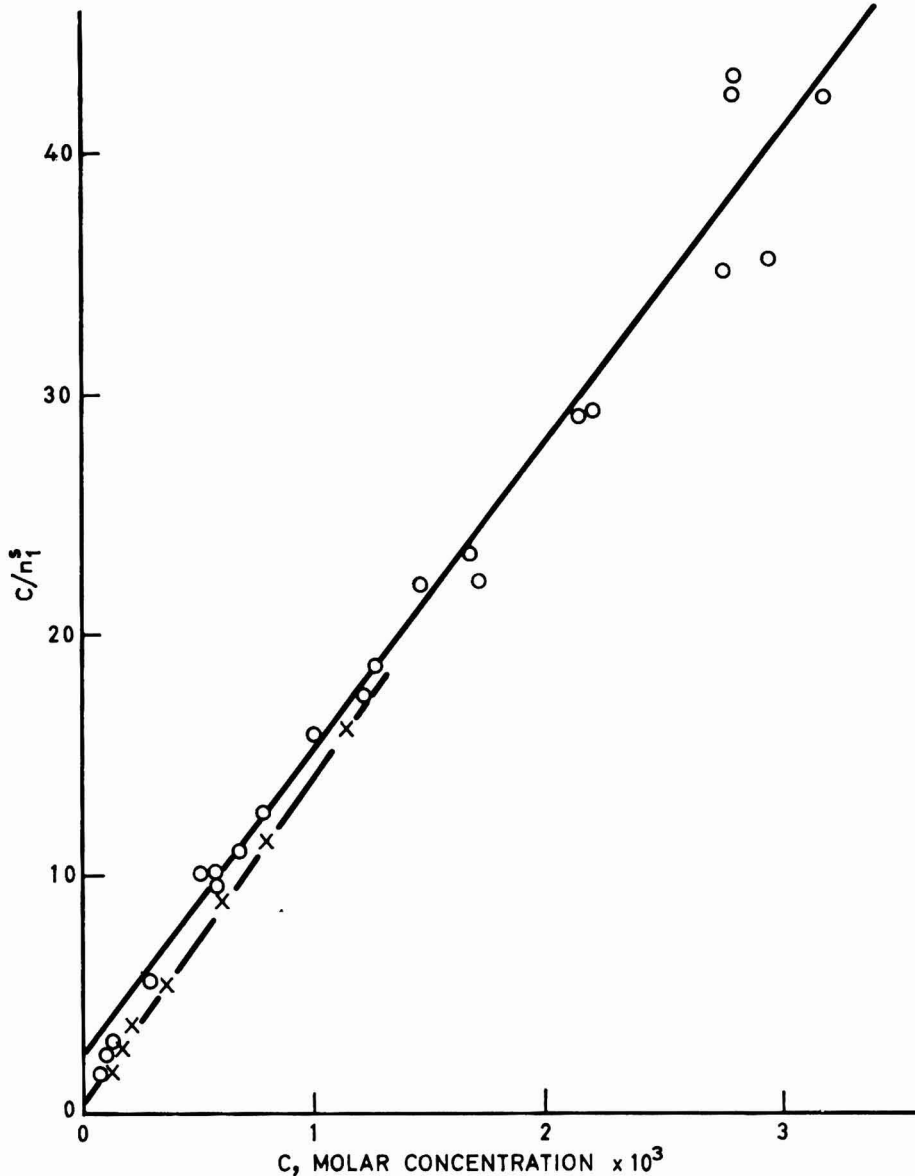


Fig. 5. c/n_1^2 against c for stearic acid, — x —, 5°C ; — o —, 25°C

to be reversible. Since the ratio gradient/intercept is equal to $(K-1).k_1$ it was possible to obtain a value of K for this region and hence a value for the free energy of adsorption from the expression,

$$-\Delta G = 2.303 RT \log_{10} K$$

A value of 6,150 cal/mole was obtained for the adsorption of stearic acid at 25°C. The linearity of the c/n_1^2 against c curves suggests that ΔG remains

reasonably constant over this region unless some compensating effect has occurred, i.e. a changing number of sites compensated by a changing free energy of adsorption.

The isosteric heat of adsorption at 25°C was calculated from the relationship,

$$\left(\frac{\partial \ln c}{\partial T}\right)_{n_1, p} = -\frac{\Delta \bar{H}_s}{RT^2}$$

The values obtained are given in Table 5, whence it can be seen that the value of $\Delta \bar{H}_s$ drops considerably as monolayer coverage is approached. The high initial value suggests that interaction is occurring between the polar head group and the surface; this is in agreement with the observations of previous workers¹⁴. The corresponding entropies of adsorption $\Delta \bar{S}_s$ were calculated from the value of ΔG and the $\Delta \bar{H}_s$ values. The results, which were restricted to the range of n_1^s between 5.5×10^{-5} and 7.29×10^{-5} moles/gram, are given in Table 5.

Table 5
Isosteric heats and entropies of adsorption for stearic acid at 25°C

n_1^s $\times 10^5$ moles/gram	$\Delta \bar{H}_s$ calories/mole	$\Delta \bar{S}_s$ calories/mole/degree
5.5	-17,430	-37.8
6.0	-15,450	-31.2
6.5	-13,140	-23.4
7.0	-9,893	-12.6
7.29	-5,521	-2.1

It is apparent from Table 5 that substantial changes of isosteric enthalpy and entropy appear to occur as a function of surface coverage, with the entropy becoming small, but still negative, towards saturation. A negative value is in agreement with expectation in view of the increase in order on adsorption at the interface. The fact that it becomes less negative with increasing coverage may well be an indication that, as saturation is approached, a positive entropy contribution arises owing to the increase in disorder which arises as n-heptane molecules are desorbed from the interface.

The curves of c/n_1^s against c for oleic and linoleic acids are given in Figs. 6 and 7. As would be expected, changes of gradient occur on these curves at the positions where steps occur on the adsorption isotherms, and the free energy

Table 6
Free energies of adsorption of acids

Acid	Temperature °C	$-\Delta G$ k.cals/mole
Stearic	5.0	6.74
Stearic	25.0	6.15
Oleic I	5.0	6.95
Oleic I	25.0	6.90
Oleic II	25.0	4.24
Linoleic I	5.0	7.03
Linoleic I	25.0	6.66
Linoleic II	25.0	4.96
Linoleic III	25.0	4.56

of adsorption is lower than for the initial region. The free energies of adsorption are tabulated in Table 6. It is notable that the free energy of adsorption for the first region is very similar for all acids, again substantiating the fact that the initial stage of adsorption is via the carboxylic head group.

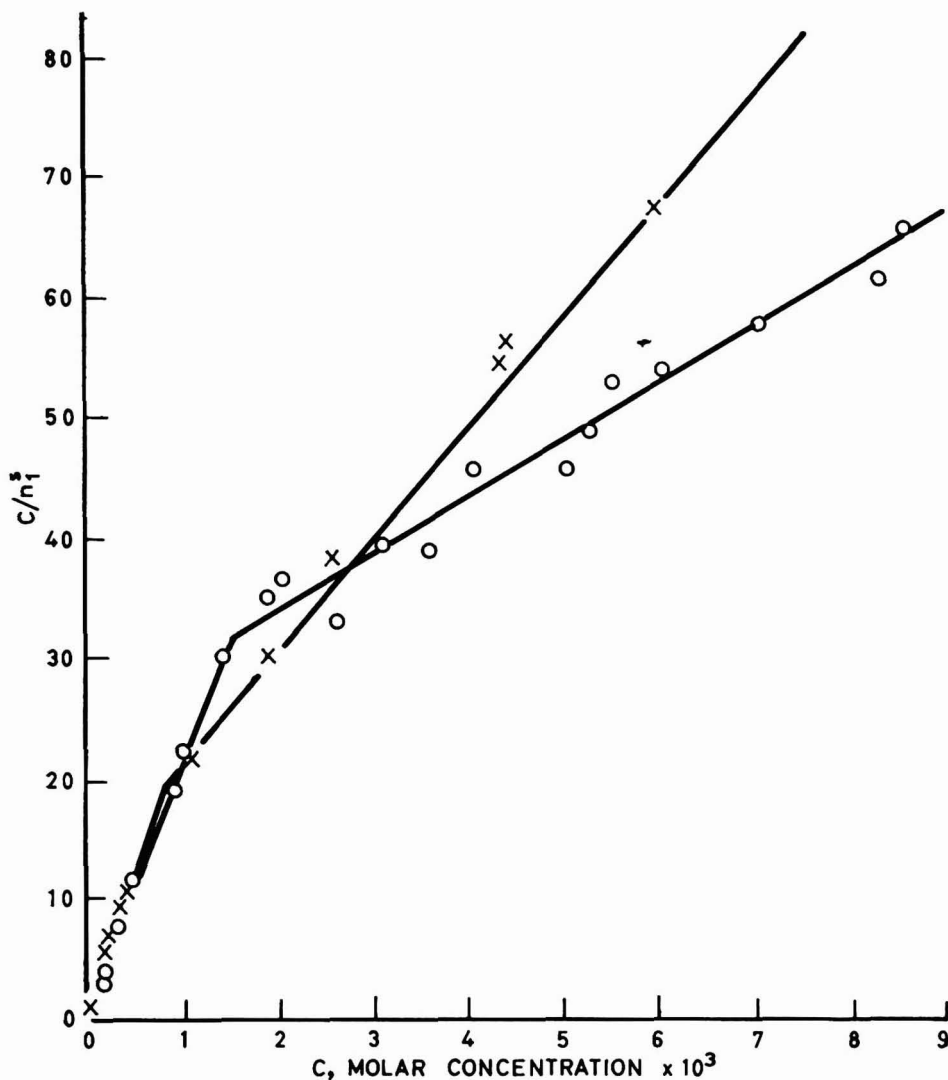


Fig. 6. c/n_i^5 against c for oleic acid, — x —, 5°C ; — o —, 25°C

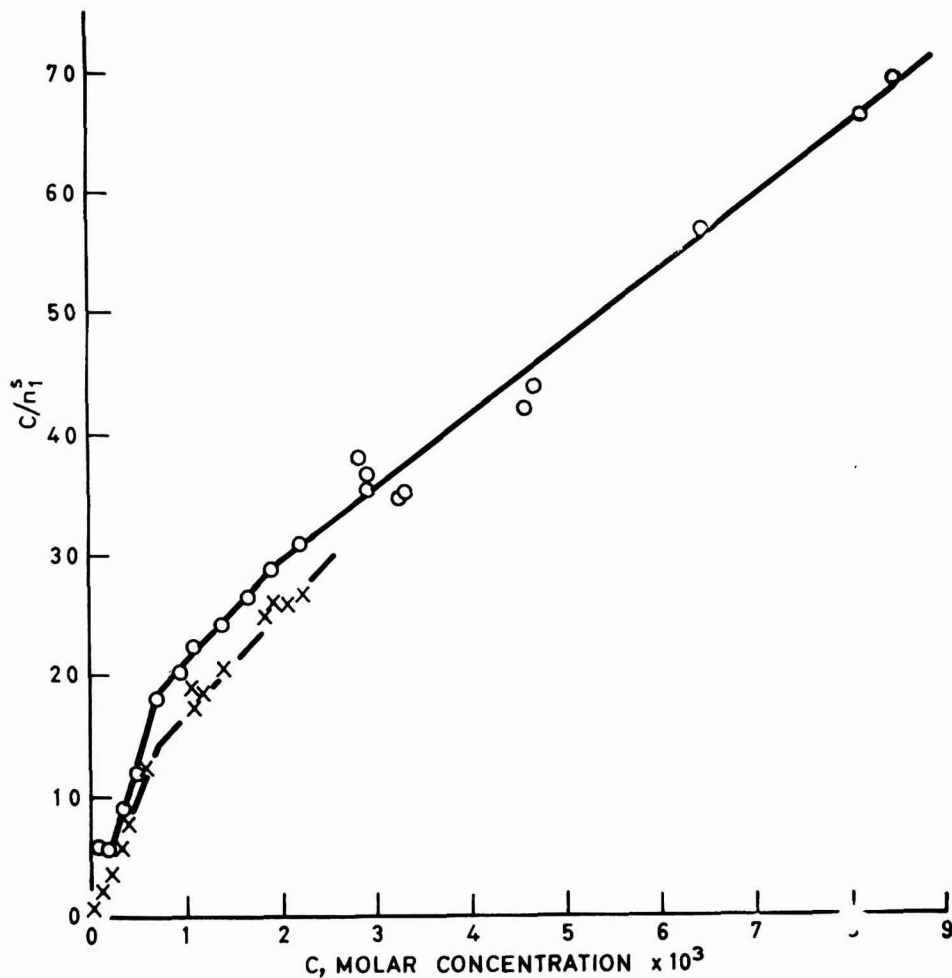


Fig. 7. c/n^2 against c for linoleic acid, — x —, 5°C ; — o —, 25°C

Acknowledgments

We wish to thank the Research Association of British Paint, Colour and Varnish Manufacturers for support of this work and for a maintenance grant to JMT. We should also like to thank Dr. V. T. Crowl for numerous helpful discussions.

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Discussion at the Scarborough Conference

DR. G. D. PARFITT (Chairman) queried the use of the Langmuir equation in adsorption from solution, as it was introduced for an essentially different process, that of adsorption in the gas phase, and made a number of basic assumptions as to the nature of the adsorption behaviour. He asked Dr. Ottewill to comment on his use of the Langmuir equation and what followed from it in describing his adsorption.

DR. R. H. OTTEWILL replied that he had been working with quite dilute solutions, and it had been shown by Everett (*Trans. Faraday Soc.*, 1964, **60**, 1803) that under these conditions the Langmuir equation could be used and it could be considered that there was an exchange on the surface. If Everett's hypothesis was accepted then the Langmuir equation could be used. He agreed with Dr. Parfitt that, in general, one had to be very cautious in applying the Langmuir equation but in this case he felt he could, with some justification, use this particular treatment.

DR. PARFITT pointed out that the hypothesis assumed a perfect adsorption process. There were many assumptions in this, and it was possible that the applicability of the equation was due to cancellations of effects working in different directions.

DR. OTTEWILL replied that the data had only been used in the very early part of the curve. They had gone as far as they could with a slightly non-ideal system. One was short of thermodynamic data on this particular system. This was one of the reasons the measurements had been carried out with unsaturated acids at two temperatures, and it did involve a great deal of effort to get accurate adsorption measurements under these conditions. With a system like n-heptane it was impossible to work at higher temperatures, as the solvent tended to evaporate, and so lower temperatures must be used. This involved quite considerable problems in the time of equilibration. He felt that, with stearic acid, it was a reasonable thing to do.

DR. H. W. TALEN suggested there was a contradiction between the conclusion of the thermodynamic analysis on page 858, where it read, "again substantiating the fact that the initial stage of adsorption is via the carboxylic head group," and the conclusions of the adsorption experiments stating a difference between the stearic acid being adsorbed only by the carboxylic group and the oleic and other unsaturated fatty acids, where a two or three point attachment by the carboxylic group and the $-C = C-$ groups was shown.

DR. OTTEWILL said that the adsorption isotherm showed quite clearly in the case of oleic acid there was a break at a concentration of 5×10^{-5} moles/g. and the experimental evidence for this was felt to be really very good. The area per molecule at this point was 47 \AA^2 , which was in very good agreement with calculations for adsorption by this particular mode. The greater part of the energy and the enthalpy would probably be associated with the interaction of the polar head group and the surface, and probably the energy of interaction of the $-C = C-$ was much lower, otherwise it would not be possible to up-end to a more vertical configuration. This would be expected to show up in the calculation of the free energy of adsorption, but it did not do so clearly.

Two conclusions could be drawn from this ; either that the experimental values of ΔG were not terribly accurate, or, alternatively, that if ΔG was subdivided into two portions, then one was so dominant that the second did not show up in the final value. The adsorption isotherm left little doubt that this must be the mode of interaction, and this was substantiated by the fact that with linoleic acid, which had two double bonds, there was a double kink on the adsorption isotherm. He felt it was disappointing that it had not shown up in the ΔG value. To summarise, it was either experimental inaccuracy or, alternatively, interaction of the double bond was very much weaker than that of the head group. There was some support from the work of Sherwood and Rybicka (*JOCCA*, 1966, 49, 648) from infrared measurements, which was in agreement with the conclusion that the double bond, in the initial stages, did lie on the surface.

MR. G. LEDERER complimented Dr. Ottewill on a very stimulating paper, and commented on the observation that the adsorption of fatty acids on the pigment surface sometimes led to considerably enhanced dispersion. This, as Dr. Ottewill had explained, was due to the adsorption of multilayers on the pigment surface. It was relevant to comment that the degree of dispersion which was achieved by the adsorption of fatty acids was substantially less than the degree of dispersion which was achieved by the adsorption of rather larger molecules, for example, alkyds. Studies were being carried out on the effects of adsorption of alkyds of increasing molecular weight on pigment dispersion, using, as the measure of dispersion, the hiding power of the resulting paints. Generally it was found that an adsorbate of smaller molecular weight adsorbed preferentially on the pigment surface. This observation could be illustrated by an experiment where a small quantity of labelled linoleic acid was added to a millbase composed of titanium dioxide and a commercial soya penta-alkyd. When adsorption equilibrium had been established, the concentration of the linoleic acid on the pigment surface was found to be ten times greater than the concentration in the rest of the vehicle. Also, generally speaking, it was found that the adsorption of small molecular weight species had a detrimental effect on dispersion as measured by hiding power. Mr. Lederer had illustrated this with two experiments.

In the first instance, 5 per cent oleic acid was added to a millbase composed of titanium dioxide and a commercial soya penta-alkyd, and it was found that the hiding power was 5 per cent deficient relative to a similar paint which did not contain the oleic acid. The second experiment was based on alkyds, and it was found that the hiding power of titanium dioxide pigment in an alkyd of high molecular weight was greater than that of the same pigment in an alkyd of low molecular weight. He then referred to experiments which were carried out using linoleic acid. The experimental technique paralleled that used by Dr. Ottewill and Dr. Tiffany. An adsorption corresponding to the first step in the adsorption isotherm of 2.98×10^{-6} (moles) linoleic acid per square metre of pigment surface was obtained. Dr. Ottewill's figure calculated in the same way, was 2.95×10^{-6} . Converted to an area, Mr. Lederer's figure was 56.7 \AA^2 per molecule ; that of Dr. Tiffany, 58 \AA^2 . This was pretty good agreement. It was interesting, however, to note that the experiments were carried out on a titanium dioxide surface which was treated with silica and alumina and had upon it 0.7 per cent of moisture.

DR. PARFITT commented that it seemed that the coating or the water was not having very much effect on the adsorption. Despite the fact that Dr. Tiffany had spent a lot of time in drying his surface, it had not affected the adsorption.

DR. OTTEWILL said that he did not think there were many comments to make in reply to Dr. Lederer. He was amazed at the agreement. It was probably gratifying but maybe highly coincidental that the agreement was so good. Perhaps it lay in the fact that both experiments used the BET method to get the surface area !

DR. W. FUNKE said that a possible concentration dependent association of fatty acid molecules in solution and its influence on the adsorption at the pigment surface had not been mentioned. It was well known from molecular weight determination of polymers that one must use rather dilute dilutions or even extrapolate to zero concentration to obtain true molecular weights. He suggested therefore that the specific change of adsorption observed with increasing concentration may also be related to association phenomena of fatty acid molecules. It was expected in this case, that these associated molecule complexes adsorbed as a whole on the pigment surface.

DR. OTTEWILL agreed with this explanation, at the high part of the isotherm ; but thought it was unlikely in the lower part of the curve. He had supported this work by infrared studies on the dimerisation of these acids in solution ; the amount of dimerisation at low concentrations appeared to be very small. He did not wish to argue about Dr. Funke's explanation on the upper end of the curve, and the suggestion may be one of the reasons why a multilayer formation was found. It was possible that this was the reason why, with linolenic acid, the curves were much less distinct. The other interesting thing about linolenic acid was that the radioactive material contained 15 per cent trans isomer. This might tend to give a more disordered packing than with all cis molecules.

He summarised that he would not dispute that aggregation may affect the upper part of the isotherm. However he felt it was unlikely at the lower part of the isotherm, particularly in view of infrared studies on solutions of these acids in normal heptane.

DR. FUNKE suggested it would be a good proposition to measure the molecular weight in the higher concentration range in order to determine whether the molecules were present in singular form or whether they were in the form of aggregates.

DR. T. DOORGEEST commented on the paper by Dr. Ottewill, the remarks made by Dr. Lederer, and remarks made by the Chairman.

He said he agreed with the choice of solvent Dr. Ottewill had used in his investigations as there was an indication that those aliphatic hydrocarbons were the least harmful solvents to be used in these types of experiment. With regard to Dr. Parfitt's question ; as long as the free energy of adsorption of the solvent molecules was negligible, and as long as solvation of the adsorbate molecules did not take place, he felt the Langmuir equation could be used without trouble.

Dr. Doorgeest's second point was an objection to part of the work. Molecules which could be oxidised rather easily had been used, and the atmosphere used was not free of oxygen. From a rough calculation there was plenty of oxygen to degrade all the oleic acid molecules and similar unsaturated fatty acids completely into other fatty acids ; and so it might be that the spreading in the results obtained may be due to oxygen.

He remarked to Dr. Lederer that he also had found that there was no relation between adsorption and dispersibility.

DR. OTTEWILL replied that they had been very conscious of the effects of oxygen, and that was why no sample of the unsaturated acid which showed any yellow colour was used. The ampoules were all opened in a nitrogen atmosphere and dissolved in heptane which had been kept in a nitrogen atmosphere. The TiO_2 , after drying, was stored in a nitrogen atmosphere. All solutions were made up in a nitrogen atmosphere. The top of the tube was flushed with dry nitrogen before the glass stopper was inserted. He felt this in practical terms was as far as one could go to remove oxygen from the system. An inhibitor—butylhydroxy toluene—had been used in some experiments. This introduced a doubt as to whether the butylhydroxy toluene

was going to adsorb as well ; since no difference had been noted in the results obtained, it was omitted in the other experiments.

He felt the other point was that the system might be much more prone to oxidation in the higher concentration regions, and this might give a partial explanation of the difficulties with oleic acid. The remarkable fact was that the reproducibility of the experiments in the lower region was good, even with different samples of oleic acid. Admittedly, a radiotracer method had been used but no difference was found with three different samples of radioactive materials. This reproducibility would not have been obtained if oxygen on that part of the isotherm was playing such a marked effect. Every effort had been made to exclude it.

DR. PARFITT said Dr. Doorgeest had commented on the choice of the solvent with respect to the oxide, and had suggested using an aliphatic solvent. Was he assuming that the aliphatic solvent was inert to the oxide surface and that if they used an aromatic solvent there might be some different effects ?

DR. DOORGEEST said that this was the case, and pointed out that there was a large difference in behaviour between aliphatic and aromatic molecules due to the interaction of the π -electrons of the aromatic molecules with the surface.

DR. PARFITT remarked that it was appreciated that the interaction between the aromatic ring and the hydroxyl groups on an oxide was very great and therefore there would be some selective adsorption here.

DR. DOORGEEST cited work done at Delft University by Professor de Boer and his collaborators. The adsorption of lauric acid on to various types of alumina had been investigated and it was found that aromatic compounds could not be used as a solvent due to the interaction of the free electrons with the surface. The conclusion was made that aliphatic compounds like *n*-hexane and *n*-heptane were the least harmful in these systems. However, there was always the possibility that there was some adsorption of the solvent molecules.

DR. PARFITT remarked that he felt that Dr. Doorgeest's point was a very important point to make, namely that there was a large difference in interaction between an aromatic and an aliphatic medium with an oxide surface, and that the adsorption behaviour and the other effects due to adsorption might be very different depending on the medium.

DR. S. WILSKA commented that pure rutile had been used in the experiments. Were the adsorption properties of commercial rutile pigments mainly determined by the properties of the rutile itself, or by the actual outer surface consisting of coating layers?

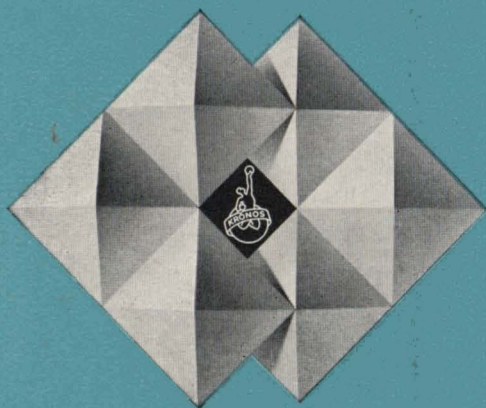
DR. OTTEWILL replied that he would say that the adsorption properties were determined by the surface.

DR. L. VALENTINE drew a parallel between some of Dr. Ottewill's work and a quite different field, that of adhesives. Later in the conference papers dealing with varying aspects of interfacial behaviour and their effect on properties would be read ; and it would be useful to show how similar types of phenomena would carry quite different technological properties. Dr. Ottewill had shown how the types of adsorption and multi-layer adsorption varied with the nature of the fatty acid and how, as the amount of unsaturation in the fatty acid was increased, there was a tendency to increase the type of multilayer adsorption. Now, scientists were very interested not just in the primary process of adsorption but also how this layer interacted with the other parts of the medium or with the interface.

Work had been done at the PRS on adhesion by Prosser and Bullett, who showed the effect on adhesion of adding fatty acids of various types to alkyls ; stearic acid

had a very harmful effect on adhesion to metal surfaces, oleic acid had a less harmful effect, and linoleic or linolenic acid had very little harmful effect on adhesion. This showed quite clearly that there was interaction between the primary adsorbed layer of fatty acid on the metal surface and the remainder of the medium. Later papers on adsorption and correlation with dispersibility showed that it was not just the first step that counted, it was the second step that counted or was more important, the interaction between the first adsorbed layer and the second one ; Dr. Ottewill's work showed how these adsorption processes would affect this very considerably. In all the discussions it must be borne in mind that these were not a single process but very complicated interactions.

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Adsorption of polyamides. Infrared measurements of the interaction with rutile and carbon black surfaces*

By R. H. Schiesser,† W. D. Schaeffer and A. C. Zettlemoyer

†Rohm and Haas Company, Springhouse, Pa., USA.

Center for Surface and Coatings Research, Lehigh University, Bethlehem, Pa., USA.

Summary

The adsorption of polyamides from solution on to rutile and carbon black has been described previously as a function of polyamide molecular weight and solvation. Various experimental methods were investigated to obtain the infrared absorption spectra of the adsorbed polyamides since the adsorbent appeared to have little influence on the specific adsorption. The problem was complicated by the pigmentary grades of adsorbents which induced marked attenuation of the radiation by scattering in the case of rutile and by absorption with carbon black. Incorporation of the adsorbents, recovered from the solution adsorption measurements, in a KBr matrix provided satisfactory transmission spectra when the spectrophotometer was equipped with a scale expander.

Reasonable agreement was obtained between solution adsorption measurements and the infrared absorption analysis of the residual polyamides using the absorbances of both the carbon-hydrogen stretching and nitrogen-hydrogen bending frequencies. The spectra of adsorbed polyamides differed from the calibration spectra principally in the disappearance of the N-H stretching frequency absorption band and a decrease in the ratio of the absorption intensities for the carbonyl stretching in the amide group to the C-H stretching frequencies in the methylene carbons. Both observations suggest that the polyamide interacts strongly with the adsorbent surfaces and completely through the amide groups in the polyamide molecule.

L'adsorption de polyamides. Les mesures à l'infrarouge de leur interaction les surfaces de rutile et de noir de carbone

Résumé

Auparavant l'adsorption, par rutile et noir de carbone, de polyamides à partir des solutions a été décrite en fonction du poids moléculaire de la polyamide et également de la solvation. On a étudié plusieurs méthodes pour obtenir les spectres d'absorption à l'infrarouge des polyamides adsorbées, puisque l'adsorbant exerce peu d'influence sur l'adsorption spécifique. L'utilisation, comme adsorbants, des types pigmentaires de rutile et de noir de carbone a compliqué le problème à cause de l'atténuation importante de la radiation diffusée que provoquait le rutile, et de l'absorption dans le cas du noir de carbone. Les adsorbants, recueillis après le mesure de l'adsorption en solution et incorporés dans une matrice de KBr, donnaient des spectres de transmission convenables à l'aide d'un spectrophotomètre doté d'un extenseur d'échelle.

On a obtenu des accords raisonnables entre les mesures de l'adsorption en solution et celles de l'adsorption à l'infrarouge des polyamides résiduelles, par l'utilisation des adsorptivités des fréquences d'allongement carbone-hydrogène et également des fréquences de déformation azote-hydrogène. Les spectres des polyamides adsorbées différaient des spectres étalons, notamment par la disparition de la bande d'absorption des fréquences d'allongement azote-

*Based on a thesis submitted by R. H. Schiesser in partial fulfilment of the requirements for the Ph.D. degree, Lehigh University

hydrogène et par la diminution du rapport des intensités d'absorption dues à l'allongement du carbonyle dans le groupement amide aux fréquences d'allongement carbone-hydrogène dans le groupement méthylénique. Toutes les deux observations suggèrent que la polyamide réagit fortement avec les surfaces de l'adsorbant, mais seulement par l'intervention de ses groupements amides.

Adsorption von Polyamiden. Infrarotmessungen von Reaktionen mit Rutil- und Gasrussoberflächen

Zusammenfassung

Die Adsorption von Polyamiden auf Rutil und Gasruss in Lösung wurde schon vor längerer Zeit als Funktion des Polyamid- Molekulargewichtes und der Solvation bezeichnet. Da das Adsorbens nur einen geringen Einfluss auf die spezifische Adsorption zu haben schien, wurden verschiedene Beispielmethode geprüft, um die Infrarotabsorptionsspektren des adsorbierten Polyamides zu erhalten. Der Pigmentcharakter der Adsorbens komplizierte das Problem, weil dieser nämlich die Bestrahlung erheblich abschwächte, und zwar im Falle Rutil durch Streuung und im Falle Gasruss durch Absorption. Einverleibung des aus der Adsorptionsmessungslösung wiedergewonnenen Adsorbens in einer K Br-Matrize ermöglichte den Erhalt zufriedenstellender Transmissionsspektren, sofern das Spektralphotometer mit einem Skalenexpander versehen war.

Befriedigende Übereinstimmung wurde erzielt zwischen Adsorptionsmessungen in Lösung und der Infrarot-Absorption des restlichen Polyamides, indem man die Absorptionsbanden sowohl der Kohlenstoff-Wasserstoff-Dehnungsschwingung, als auch der Stickstoff-Wasserstoff-Deformationsschwingung benutzte. Die Spektren der adsorbierten Polyamide unterschieden sich von den Vergleichsmessungen hauptsächlich dadurch, dass das N-H verlängernde Frequenzabsorptionsband verschwand, und sich das Verhältnis der Absorptionsstärken für die Carbonyldehnung in der Amidgruppe zu den C-H Dehnungsschwingungen in der Methylen-Gruppe verminderte. Beide Beobachtungen legen es nahe, dass das Polyamid stark mit den adsorbierenden Oberflächen reagiert, und dass diese Reaktion ausschliesslich über die Amidgruppen im Polyamidmolekül erfolgt.

Адсорбция полиамидов. Инфракрасные измерения взаимодействия с рутиловыми и сажевыми поверхностями

Резюме

Адсорбция полиамидов из раствора на рутиле и саже описывалась раньше как функция молекулярного веса полиамида и сольватации. Были исследованы различные экспериментальные методы для получения инфракрасных спектров абсорпции адсорбированных полиамидов т.к. адсорбент повидимому не проявлял сильного влияния на удельную адсорбцию. Задача усложнялась пигментарными градациями адсорбентов, которые причиняли заметное затухание радиации рассеянием в случае рутила и абсорпцией в случае сажи. Применение адсорбентов восстановленных из измерений адсорбции раствора в матрице KBr, доставило удовлетворительные спектры трансмиссии когда спектрофотометр был снабжен расширительной шкалой. Удовлетворительное согласие было получено между измерениями адсорбции раствора и анализом инфракрасной абсорпции остаточных полиамидов, используя абсорпции частот как углеродоводородного растяжения так и азотно-водородного изгибания. Спектры адсорбированных полиамидов отличались от спектров калибровки главным образом в исчезновении абсорпционной полосы частоты растяжения N-H и в понижении отношения абсорпционной интенсивности карбонильного растяжения в группе амидов к частотам растяжения C-H в метиленовых углеродах. Оба факта свидетельствуют о том что полиамид сильно взаимодействует с поверхностями адсорбента и полностью через группы амидов в молекуле полиамида.

Introduction

The interactions among polyamides, 1850 to 8000 average molecular weights, solvents, and polar and non-polar adsorbents have been characterised¹ based on solution viscosity and adsorption measurements. The polyamides apparently exist as flexible coils in alcohol solutions, in so far as the limiting viscosity numbers could be related directly to the polyamide molecular weight by the relationship^{2,3}

$$[\eta] = KM^\alpha$$

Values of α increased from 0.42 to 0.51 on changing solvents from n-propanol to n-butanol, the magnitudes suggesting that the molecules were behaving as solvated spheres.

The adsorption isotherms on a surface treated rutile and carbon black were determined from ultraviolet spectrophotometry measurements of polyamide concentration differences between initial and equilibrated solutions. The levels of the Langmuir-type adsorption isotherms increased with increasing polyamide molecular weight and decreased with improved solvation. The dimensions of the adsorbed polymer molecules estimated from nitrogen surface areas of the adsorbents and Langmuir plots of the solution adsorption were considerably smaller than the solution hydrodynamic radii, but maintained proportional relationships on both adsorbents. In view of the dissimilarity of the adsorbent surfaces, and the similarity of molecular areas, the interactions of the polyamides with the two types of surfaces were of interest.

Infrared absorption spectrophotometry of recovered adsorbent samples with associated adsorbed polyamide was undertaken to confirm the levels of solution adsorption and to provide information as to possible structures of the adsorbed polyamide films.

The first infrared study of adsorbed polymers was reported by Fontana and Thomas⁴ and continued by Fontana⁵. These authors studied alkyl methacrylates adsorbed on silica, and observed a splitting of the carbonyl band which was interpreted as a perturbation of the adsorbate electronic structure. In other words, a fraction of the carbonyl groups was hydrogen bonding with surface hydroxyl groups. Measurements of band intensities for the normal and shifted carbonyl bands led to the conclusion that approximately 40 per cent of the monomer segments were interacting with the surface.

Infrared absorption spectrophotometry has been applied much more extensively to the study of the bonding of the adsorbed phase in gas-solid binary solution-solid interactions. Studies have been reported⁶ of the solution adsorption of amines, ketones and ethers on porous silicate adsorbents. More recently, infrared techniques have been applied to the evaluation of adsorbed fatty acid carboxyl group interactions with inorganic surface coatings on titanium dioxide pigments^{7,8}.

Experimental

Adsorbents

Two samples of Elf 5 carbon black were used in the studies. Elf 5-1 was available from stock in this laboratory. After this supply was exhausted, another sample was obtained from the Special Black Division of the Cabot Corporation and

designated Elf 5-2. The surface areas as determined from BET treatment of nitrogen adsorption measurements at -195°C were 109.3 and 96.3 m^2/g for Elf 5-1 and Elf 5-2, respectively. Prior to all adsorption measurements, the samples were dried at 110°C for 18 hours.

The rutile titanium dioxide used in this investigation was R-110, supplied by the Pigments Division of E. I. du Pont Company. The composition as specified by the manufacturer is 97 per cent TiO_2 , 0.5-1.5 per cent Al_2O_3 and 0.0-1.0 per cent SiO_2 . The surface area of R-110 was 8.8 m^2/g . The rutile samples also were dried at 110° for 18 hours prior to the solution adsorption experiments.

Polyamides

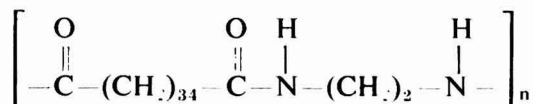
The polyamide resins were supplied by the Lawter Chemical Company and S. C. Johnson Company. The resins were prepared from the reaction of dimer acid with ethylene diamine. The dimer acid was a viscous aliphatic (principally C_{36}) dibasic acid.

The properties of the polyamide resins are summarised in Table 1. The molecular weight values were determined on a Model 301 Mechrolab Vapor Pressure Osmometer, for which n-propanol and isopropanol were used as

Table 1
Properties of polyamide resins

Polyamide	Supplier	Acid value	Amine value	MW
A	Lawter	3.4	less than 6	1855
C	Lawter	2.0	less than 6	3900
E	S.C.J.	4.9	3.43	8050

solvents. The condensed unit structure



has a molecular weight of 590. On this basis Polyamides A, C, and E should contain 3.1, 6.6 and 13.6 condensation units, respectively. The model is idealised somewhat since the hydrocarbon chains are known to be branched⁹.

Procedures

Reference spectra of polyamide films were obtained on sodium chloride discs 25 mm diameter and 4 mm thickness. Multiple depositions from dilute alcohol solution were used to develop films of suitable thickness. The solvents were evaporated at 50°C and reduced pressure.

The technique which proved useful for the analysis of adsorbate-adsorbent complexes was the potassium bromide (KBr) pellet technique. IR quality KBr was obtained from the Harshaw Chemical Co. The manufacturer supplied IR spectra of the samples in the range of 2-15 microns. The spectra showed only two minor absorption peaks due to adsorbed water centred at 2.9 and 6.0 microns. The KBr powder was dried before use at 150°C for several days and

stored in a desiccator over phosphorus pentoxide. The exposure of this dried powder to the atmosphere was minimised in all subsequent operations. Spectra obtained from a sample of KBr dried in this manner showed a negligible amount of residual water.

Samples were first prepared by adding a few milligrams, weighed to ± 0.1 mg, of the substance whose spectrum was desired to 300 mg of KBr and mixing the two solids for 20 to 30 seconds in a Wig-L-Bug Dental Vibrator. The procedure was later modified to reduce scattering losses in the sample due to pigment agglomerates.

The modified mixing procedure consisted of adding known weights of recovered adsorbent to KBr and grinding thoroughly in an agate mortar and pestle under carbon tetrachloride. The extensive grinding of a sample with KBr could not be done in the atmosphere because of the hygroscopic nature of KBr. Carbon tetrachloride was a suitable mulling liquid since it did not dissolve or desorb polymer from the adsorbent, and also because it was inactive in the regions of the polymer infrared absorption bands. The mulls were ground for approximately 15 minutes. The carbon tetrachloride was removed by vacuum drying, leaving a sample well-dispersed in KBr. In some cases, aliquots of the initial KBr dispersion were diluted with additional KBr and reground under carbon tetrachloride.

The grinding and drying operations were followed by the pelletising process. A 16 mm diameter Limit Research Corporation stainless steel die equipped with optically polished discs and a vacuum connection was used to form the pellets under pressure. The KBr dispersion was added to a heated die which was then assembled and placed in a Carver Hydraulic Press. The cell was evacuated with a mechanical vacuum pump for a period of one minute. Then 20,000 psi of pressure was applied for a period of two minutes while the vacuum was maintained. This procedure produced a disc approximately 1 mm thick which could be handled easily. Pellets of pure KBr were also prepared during each experiment for use as reference standards. All pellets were stored in a desiccator over phosphorus pentoxide in order to minimise water absorption.

The infrared measurements were made on a Perkin-Elmer Model 21 recording infrared spectrophotometer. Examination of the pellets, prepared by the method described above and containing adsorbent plus adsorbed polyamide, gave extremely weak absorption bands in the infrared range. Only after equipping the spectrophotometer with a Perkin-Elmer Ordinate Scale Expander, Model 021-0367, were the band intensities adequate for quantitative analysis. The unit provided continuously variable expansion from 1X to 5X, and four step-wise expansions of 1X, 5X, 10X and 20X. Most of the reported measurements were made at both 1X and 10X expansion and appropriate reductions in scanning speed.

Results

The major features of the infrared spectra from 2 to 15 microns for polyamide A, C, and E films on NaCl are illustrated in Fig. 1. The tracing is restricted to the two regions 2.8 to 3.9 and 5.8 to 7.3 microns because they contain most of the absorption bands of interest. A summary of the assignments of specific absorption bands of interest and their intensities is given in Table 2. In general,

the assignments resemble those described by Kagarize and Weinberger for Type 6 nylon¹⁰.

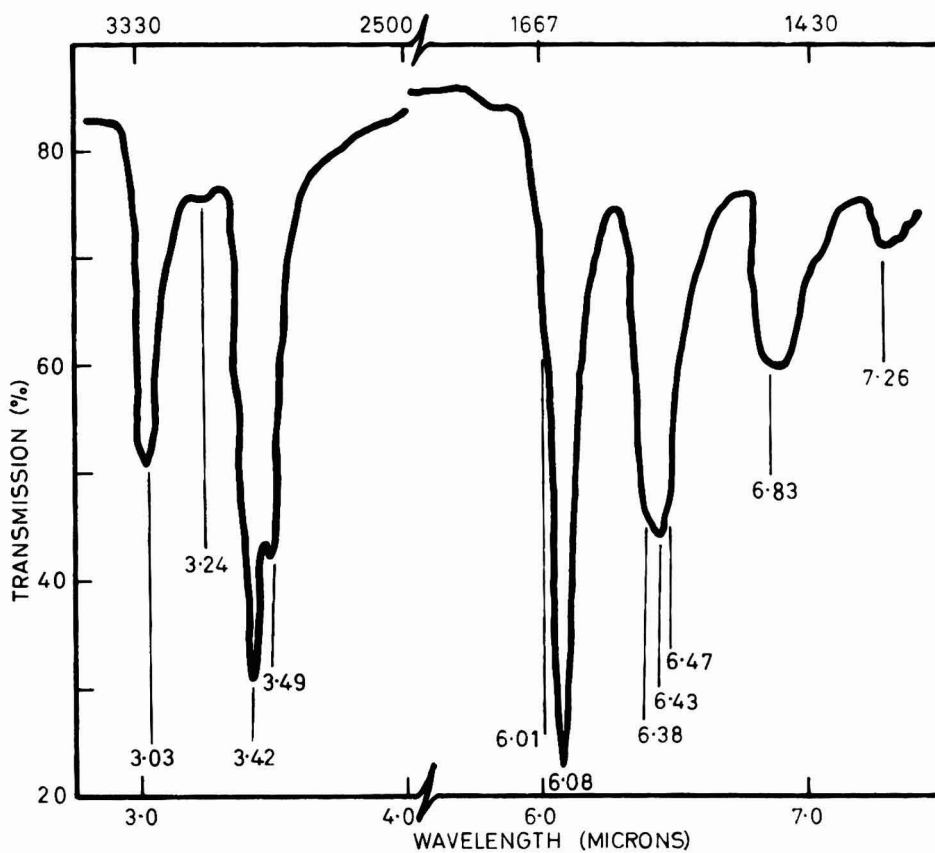


Fig. 1. Infrared spectrum of polyamide E film.

Table 2
Frequency assignments for polyamides

Band	Wave length (μ)	Wave number (cm^{-1})	Intensity
N-H stretch from N-H and NH_2 ..	3.04	3289	s
N-H stretch from NH_2	3.25	3077	w
C-H stretch from CH_2	3.43, 3.51	2915, 2849	s
C = O stretch from amide	6.03, 6.08	1658, 1645	m, s
N-H bend from amide	6.38, 6.45	1567, 1552	m, vs
C-H bend from CH_2	6.85, 7.28	1460, 1374	m

No major differences were observed for recorded spectra of the polyamides between free film samples and KBr-mulled samples at 1 per cent polymer concentration. However, when samples were investigated at the 0.03-0.05 per

cent polymer concentration with the use of scale expansion, splitting of the bands was observed, an occurrence which first suggested an interaction between polymer and KBr. An example of a polyamide-KBr matrix spectrum measured with scale expansion is shown in Fig. 2 for Polyamide A.

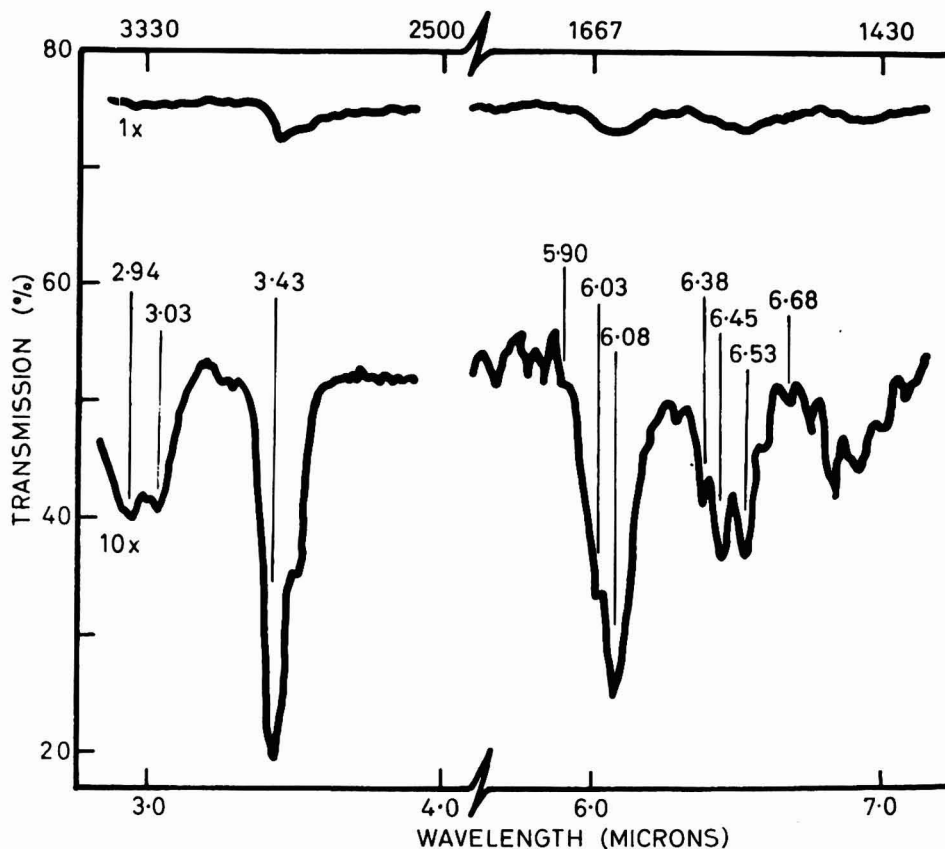


Fig. 2. Infrared spectrum of polyamide A-KBr matrix

The significant changes between these spectra and those obtained from free films occurred in both the N-H stretching band and two amide bands. Amide I is the carbonyl stretching frequency centred at 6.08 microns, and amide II is the N-H bending band centred at 6.45 microns.

A quantitative analysis of Polyamide E absorption bands was undertaken at various polymer concentrations dispersed in KBr. The results provide a direct comparison with solution adsorption measurements. The baseline method¹¹ was used to measure peak intensities on the spectra. The Beer-Lambert calibration plots illustrated in Fig. 3 were obtained for the major absorption peaks and the extinction coefficients, a_m , listed in Table 3 were calculated from the slopes of the lines.

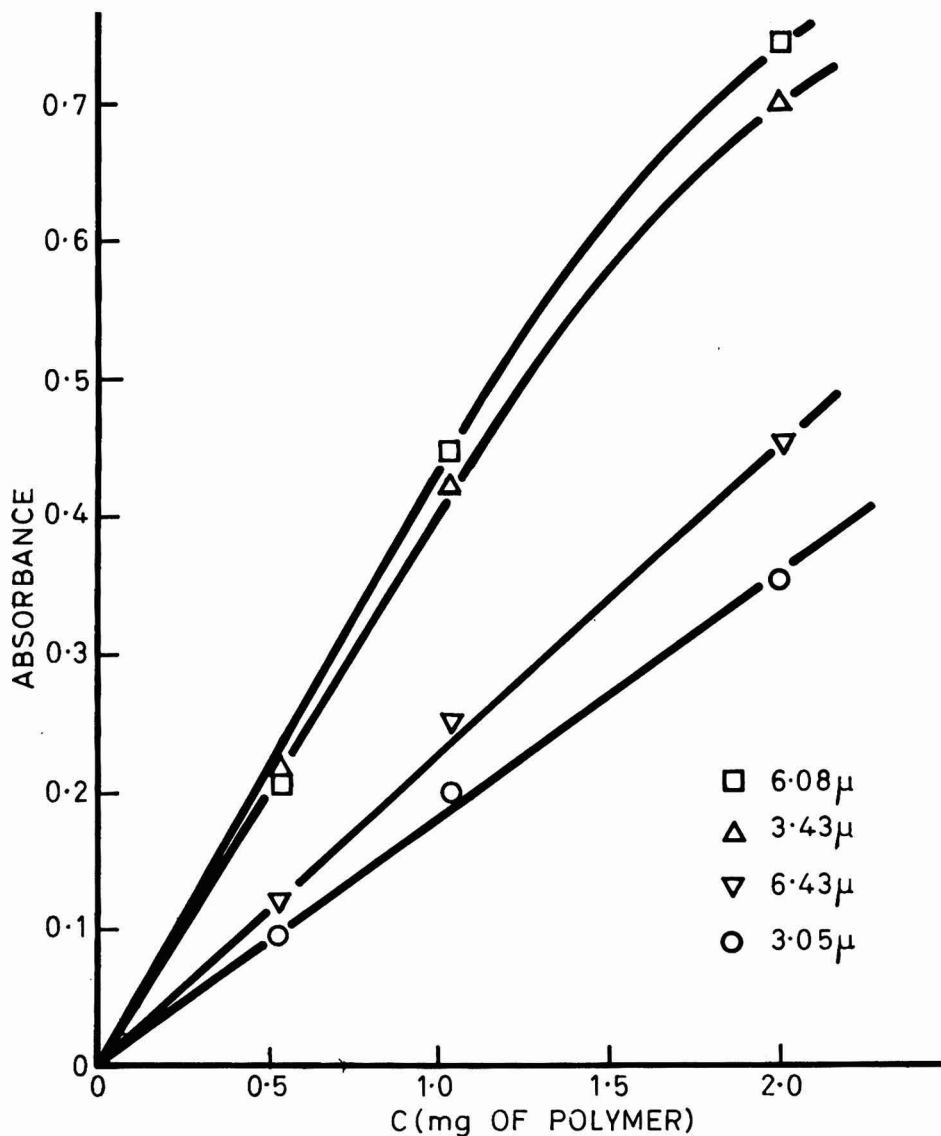


Fig. 3. Beer-Lambert calibration for polyamide E

Table 3
Extinction coefficients for Polyamide E

Wave length (μ)	a_m
3.05	0.185
3.43	0.408
6.08	0.430
6.45	0.230

Infrared analyses were performed on most of the polyamide-adsorbent combinations. The spectrum of Polyamide A adsorbed on Elf 5-2 from *n*-butanol solutions is shown in Fig. 4. The KBr matrix contained between

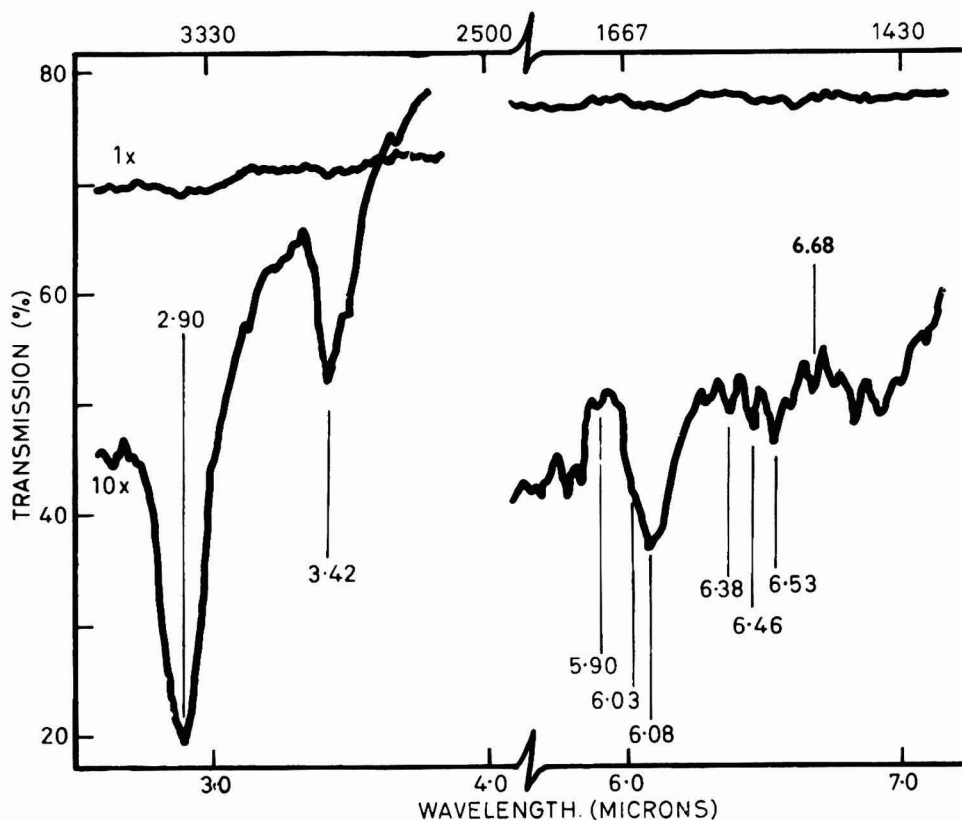


Fig. 4. Infrared spectrum of polyamide A adsorbed on Elf 5-2

110 and 120 micrograms of polyamide adsorbed on Elf 5-2, as estimated from a solution adsorption value of 104.3 mg/g. The notable features of the spectrum, recorded at 10X expansion, are the presence of absorption bands at 6.08 microns, indicative of C = O stretch, and the absence of an absorption peak at 3.04 microns where the N-H stretching band normally occurs. Infrared absorption spectra were also recorded for Polyamide A adsorbed on rutile from *n*-propanol. An example is shown in Fig. 5 at 10X expansion for a sample containing 3.5×10^3 micrograms of polymer-adsorbent dispersed in approximately 300 mg of potassium bromide. The amount of polymer adsorbed from solution was 9.0 mg/g. Strong absorption peaks were obtained again at 3.43, 6.08 and 6.45 microns, and the peak shape corresponding to the N-H stretching band at 3.05 microns was changed drastically.

Figs. 6 and 7 illustrate the infrared spectra for samples of Polyamide C and E adsorbed on Elf 5-2. The samples contained 3.2 and 6.3×10^2 micrograms of polyamide-adsorbent, respectively. The polyamide solution adsorption

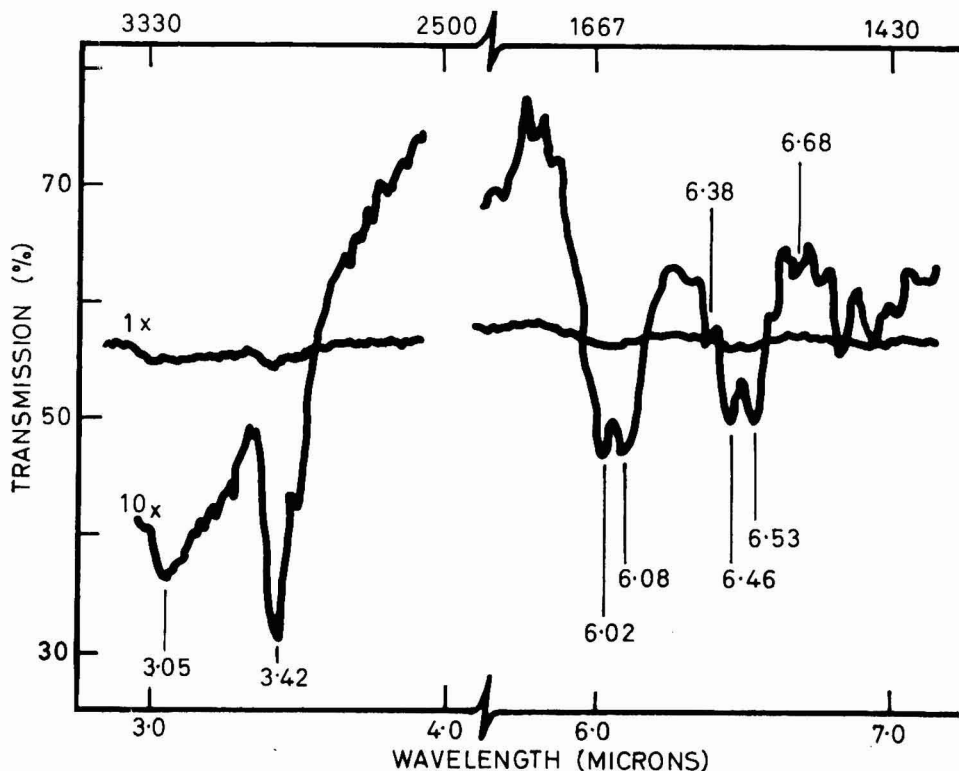


Fig. 5. Infrared spectrum of polyamide A adsorbed on rutile

on these samples was 196 mg/g and 181 mg/g, respectively. The major absorption peak apparent in the 3-4 micron region is the C-H stretch at 3.43 microns. Only in Fig. 7 is there a suggestion of an inflection corresponding to the N-H stretching band at 3.05 microns. The carbonyl stretch at 6.08 microns is the strongest band present, but the peaks appear to broaden in both spectra. Since absorption peaks due to the presence of residual water in potassium bromide are known to occur at 2.9 and 6.1 microns, the broadening of the carbonyl band at 6.08 microns may be due to interference from water¹².

The extinction coefficients summarised in Table 3 provide the basis for the calculation of Polyamide E concentrations on the adsorbent samples selected for infrared analysis. The quantitative calculations are based on C-H band

Table 4
Polyamide E adsorption
from infrared and solution measurements

Adsorbent	IR Surface concentrations (mg/g)	UV Solution adsorption (mg/g)
Rutile	34	27
Elf 5	151	181

(3.43 micron) intensity for the Polyamide E-rutile system and on the N-H band (6.45 micron) of the amide group for the Polyamide E-Elf 5 system. Table 4 summarises the Polyamide E concentrations as calculated from the infrared spectra and solution adsorption measurements.

Absorbances ($\log I_0/I$) also were calculated for the major absorption peaks of both pure and adsorbed polyamides on rutile and carbon black. The values are summarised in Table 5. Since the absorbance is dependent upon the concentration of the absorbing group, the values listed in Table 5 vary widely, because of differences between the samples. The relative ratios of absorbances for two absorption bands in a given polyamide spectrum should be characteristic. Should the ratio change from one environment to another, a perturbing influence due either to the KBr matrix or adsorbent may be involved.

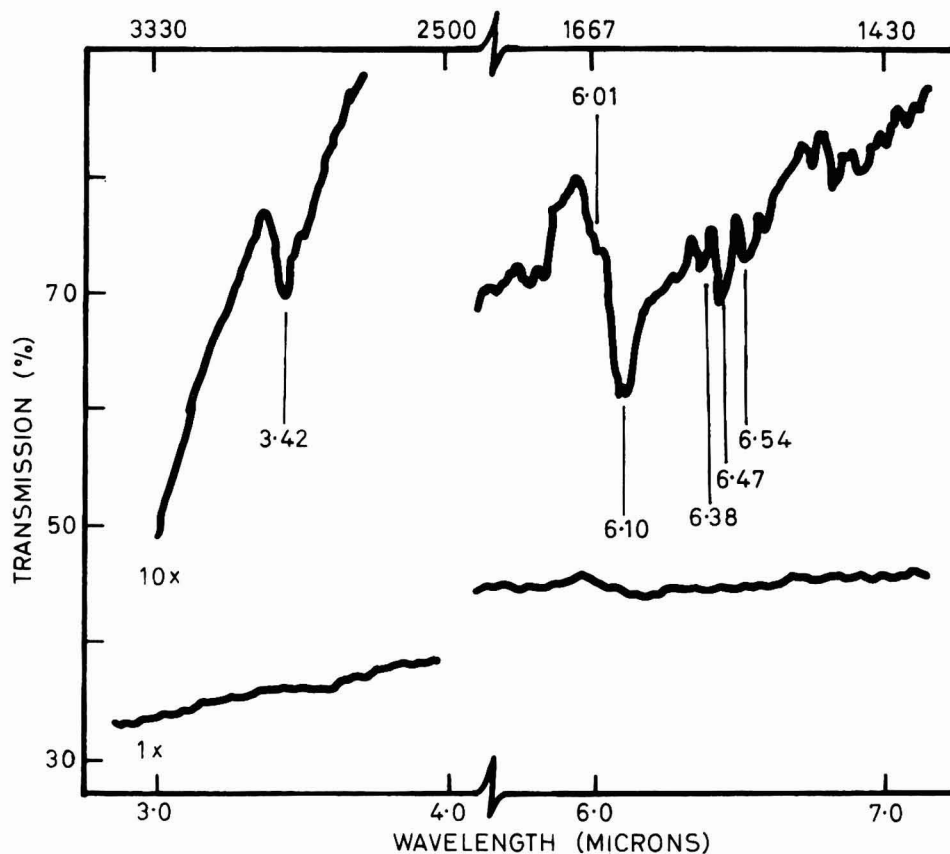


Fig. 6. Infrared spectrum of polyamide C adsorbed on Elf 5-2

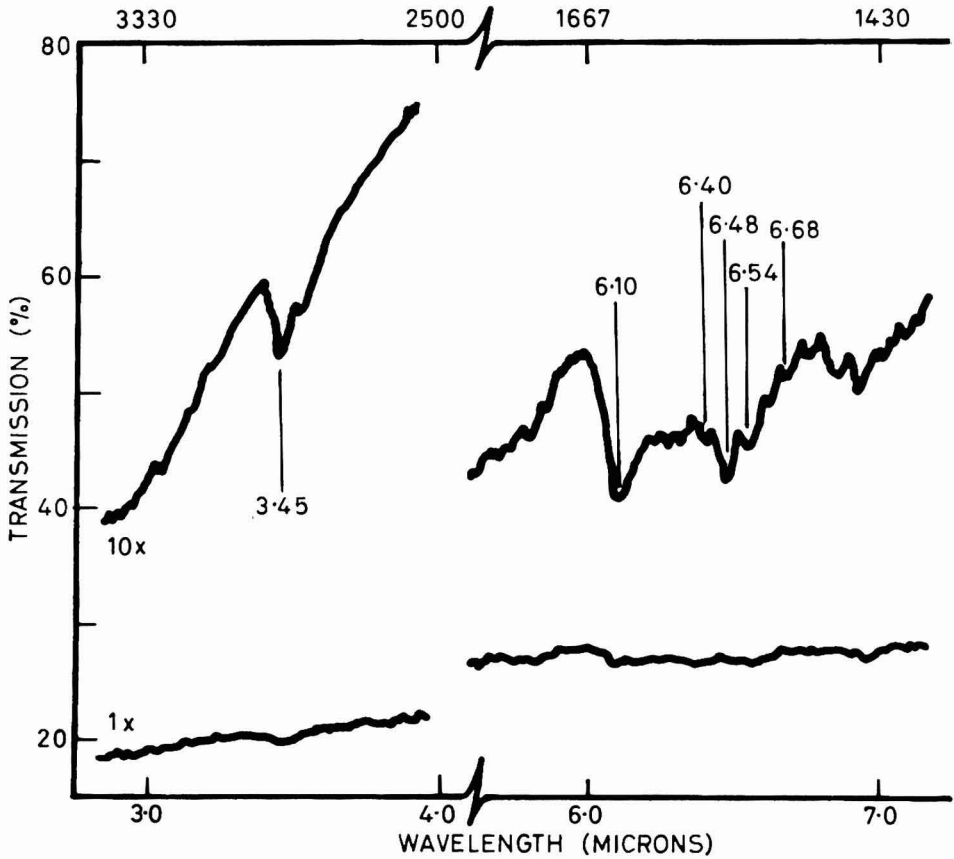


Fig. 7. Infrared spectrum of polyamide E adsorbed Elf 5-2

Table 5

Absorbances calculated from infrared spectra of pure and adsorbed polyamides

Wave length	3.05	3.43	6.08	6.45
Polyamide A	0.010	0.020	0.018	0.011
Polyamide C	0.043	0.094	0.101	0.053
Polyamide E	0.012	0.029	0.032	0.019
Polyamide A on rutile	—	0.015	0.013	0.009
Polyamide E on rutile	—	0.051	0.035	0.023
Polyamide A on Elf 5	—	0.010	0.008	0.004
Polyamide C on Elf 5	—	0.020	0.022	0.017
Polyamide E on Elf 5	—	0.019	0.020	0.021

Discussion

The modification of typical polyamide spectra as in Fig. 1 when present at very low concentrations either in KBr alone, Fig. 2, or when introduced with adsorbent in KBr, Figs. 4-7, can be due to a number of causes. A number of characteristic amide absorption bands are known to split and shift with solution dilution.^{13,14} Crystalline α -naphthalene acetamide has been demonstrated to undergo structural changes with increased time of mulling in KI¹⁵. Moisture adsorption by KBr was the most troublesome potential problem because bands at 2.95 and 6.1 micron could interfere with known amide absorption frequencies.

The potential difficulty of isolating the N-H stretching band at 3.03 microns from the 2.94 O-H stretching band was illustrated best in Fig. 2 where the overlap and band distortion could be distinguished readily. Introduction of the adsorbents with adsorbed polyamides compounded the problem.

The spectra of carbon black with adsorbed polyamides, Figs. 4, 6 and 7, contain absorption bands of varying widths, centred at 2.90 in Fig. 4, and little if any trace of the N-H stretching band at 3.04 microns. Slight changes of curvature on steeply rising band shoulders at 3.04 microns in Figs. 4 and 7 are the only traces of any residual N-H stretching absorption.

The spectrum in Fig. 5 of rutile containing adsorbed Polyamide A, on the other hand, contains a broad band centred at 3.05 microns. Very similar spectra were obtained with the other polyamides adsorbed on rutile. The difference in band shapes between Figs. 5 and 2 suggested that the apparent absorption at 3.05 microns was due to adsorbed water on the KBr. The maximum in the 1X spectrum at 2.90 to 2.95 microns in Fig. 5 indicated that the water content of the KBr window in the reference beam was greater than in the sample window. The edge of the resulting 'reverse absorption band' consequently was responsible for the apparent wide band at 3.05 microns on the 10X spectrum.

The apparent disappearance of the N-H stretching absorption band actually serves as reasonable evidence for a shift to shorter wave length (greater wave number). The infrared study of butyl ethanamide and its derivatives demonstrated that the N-H stretching bands corresponding to the observed polyamide absorption at 3.03 and 3.23 microns shifted in dilute solution to a band at 2.91 microns,¹³ an ideal location for interference with the O-H absorption band in the present study. The feature of this comparison, however, is that the shorter wave length absorption by butyl ethanamide is characteristic of the N-H stretching frequency unperturbed by hydrogen bonding. If the situation is analogous in the polyamides and the 3.03 micron absorption band is characteristic of the intra- and intermolecular hydrogen bonded N-H stretching frequency, adsorption of the polyamides' functional groups restricts the ability to form intramolecular hydrogen bonds. In retrospect this may not be too surprising if the four atom amide group is planar and adsorbed parallel rather than perpendicular to the surface. The perpendicular configuration should promote hydrogen bonding, particularly with the rutile adsorbent; whereas adsorption parallel to the surface should hinder energetically the amide groups from adjacent chain segments approaching one another sufficiently closely to form hydrogen bonds.

The fact that the major Polyamide E absorption bands followed the Beer-Lambert relationship in Fig. 3 over a reasonable concentration range does not guarantee that the responsible absorbing groups are behaving independently of the KBr matrices. In view of these reservations, the agreement is good between Polyamide E adsorption on rutile and carbon black calculated from infrared extinction coefficients and ultraviolet spectrophotometric solution measurements. The results listed in Table 4 were sufficiently promising to apply the KBr technique to polyamide desorption studies now in progress.

While the two examples in Table 4 provide reasonable agreement, inconsistencies can be obtained readily in calculated polyamide adsorption if absorbances are used from several bands in the spectrum of a given adsorbent-adsorbate system. The problem can be illustrated by calculating the absorbance ratio for any two of the several absorption bands with values listed in Table 5. Typical ratios are listed in Table 6 for the amide I, a carbonyl stretching frequency, and the amide II band, an N-H bending frequency. The C-H stretching band absorbance at 3.43 microns was chosen as the reference because the frequency and extinction coefficient were least likely to be perturbed by the adsorption process. The amide I and II bands, on the other hand, are very sensitive in monosubstituted amides, both in frequency and intensity, to changes in state and concentration.^{13, 14} Rather extensive analyses have been reported on the characterization of these bands because of the interest in the structural analysis of polypeptide chains.

Table 6
Absorbance ratios calculated from infrared spectra
of free and adsorbed polyamides

Polyamide	A(6.08)/A(3.43)	A(6.45)/A(3.43)
A	0.90	0.55
C	1.07	0.57
E	1.10	0.66
A on rutile ..	0.87	0.60
E on rutile ..	0.69	0.45
A on Elf 5 ..	0.80	0.40
C on Elf 5 ..	1.10	0.85
E on Elf 5 ..	1.05	1.10

The first set of absorbance ratios listed in Table 6 are for the polyamides dispersed in KBr. The absorbance ratios for both the amide I and II bands relative to the C-H stretching band increase with increasing polyamide molecular weight.

The corresponding absorbance ratios for the adsorbed polymers depended upon the particular adsorbent. Both absorbance ratios for Polyamide E on rutile are less than the ratios for free (unadsorbed) Polyamide E. The decrease in absorbance ratios can be explained by one or more means: (1) fractionation of molecular weights during the adsorption process; (2) shift of an absorption band and change in intensity due to dilution or deaggregation during adsorption; or (3) preferential interaction between one or more of the polyamide functional groups and the hydroxyl groups known to be present on the rutile

surface.¹⁶ The first possibility, fractionation of polymers during the adsorption process, has been eliminated by viscosity studies reported earlier¹ which demonstrated that higher molecular weight polyamide fractions were preferentially adsorbed by rutile. Therefore, the decrease in the absorbance ratios for the adsorbed Polyamide E cannot be attributed to selective adsorption of the lower molecular weight polyamide fractions.

The 6.08 micron band is characteristic of the $C=O$ stretching frequency in monosubstituted amides; however, two equal intensity components have been characterised in the N-butyl ethanamide spectra,¹³ each of which is within 2 cm^{-1} of the shoulder at 6.03 microns and major peak at 6.08 microns in the Polyamide A spectrum in Figure 2. Dilution of N-butyl ethanamide in a non-polar solvent caused the amide I band to shift to 5.93 microns and slightly more in the case of N-methyl acetamide.¹⁴ The closest analogue to this shift in the polyamide spectra is an inflection of variable intensity which appears at 5.90 microns.

The relative absorption intensities at the three frequencies associated with the amide I band in the polyamides varies with both polyamide molecular weight and adsorbent. No attempt has been made to treat the intensities quantitatively because of possible interference from adsorbed water on KBr. The intensity of the 6.03 micron band relative to the 6.08 micron band is greatest for the lowest molecular weight Polyamide A. Adsorption of the Polyamide A on to rutile promoted the relative intensity of the 6.03 micron band without significantly affecting the absorbance ratio of the 6.08 band to the 3.43 band as indicated in Column 2, Table 6. Adsorption of Polyamide E on rutile markedly reduced the relative intensities of both amide I and amide II bands. With respect to the amide I band some shift may have occurred to 5.90 microns since the band, though weak, is better developed than in any other spectra of adsorbed polyamides.

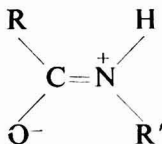
The similarities between the amide I absorbance ratios for the adsorbed polyamides on carbon black and for the corresponding polymers in KBr suggested that simple dilution during adsorption was not the major reason for spectral shifts observed in the polyamide-rutile samples. Specific interaction between the amide carbonyl group and rutile was another possible cause. Fontana and Thomas⁴ used infrared spectrophotometry to investigate adsorbed mono- and di-esters as well as polymethylmethacrylates on equilibrated silica suspensions. The development of a new carbonyl band at a lower wave number was observed due to the group interacting with the silica surface. The frequency shifts were $20\text{-}30\text{ cm}^{-1}$ and the band intensities provided estimates of the numbers of free and adsorbed segments.

Isolation of the adsorbents in this investigation and incorporation into KBr matrices eliminated the possibility of identifying the solvated and adsorbed groups. Even the solvated groups in solution which belonged to adsorbed molecules could collapse to either polymer or adsorbent surface during removal from suspension and drying. Nevertheless, the present work indicates that the KBr technique can be sufficiently sensitive to characterise various energy states of the $C=O$ stretching band in adsorbed polyamides.

The third column in Table 6 was based on the absorbance ratios of the amide II band, 6.45 microns, to the C-H stretching band. The ratios increased

slightly with polyamide molecular weights when dispersed in KBr. The response to adsorption was more varied than that of the amide I band. The ratio decreased for Polyamide E on rutile very similarly to the behaviour of the amide I band. On carbon black, the response varied with polyamide molecular weight, the ratio for the lowest molecular weight decreased, and increased for the two highest molecular weights. The mixed response to adsorption may not be too surprising in view of the several factors influencing the frequency and intensity of this band.

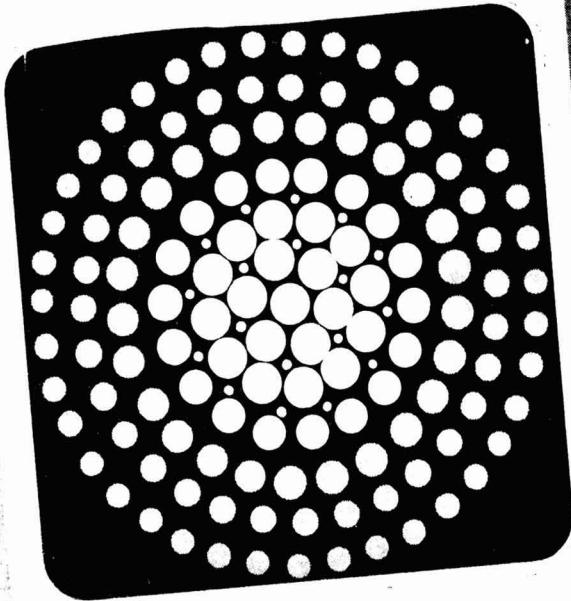
The 6.45 micron band disappears on disubstitution of amides and is generally attributed to N-H in-plane bending in monosubstituted amides.¹¹ A major contribution in determining the frequency is derived from the resonance form of the amide group¹⁷



as well as the C-R and N-R' bond vibrations.¹⁴ The band frequency also is sensitive to dilution and changes of state. An analysis of the amide II band structure in diformylhydrazine and its deuterated analogue led Miyazawa, Shimansuchi and Mizushima¹⁴ to the conclusion that the band frequency in the non-deuterated form is also sensitive to the vibration stretching frequency of the N-H bond. On this basis, the observed effects of polyamide adsorption on the N-H and C=O stretching frequencies may be reflected in the amide II band structure and absorbance.

The central amide II band for polyamide films on NaCl, Figure 1, was located at 6.43 microns and appeared to have poorly resolved inflections on both sides. The KBr spectrum of Polyamide A in Figure 2 has resolved three peaks in this region, one of low intensity at 6.38 microns and two of approximately equal intensity at 6.45 and 6.53 microns. A similar set of bands was reported in the spectra of N-butyl ethanamide and its derivatives.¹³ Bands in the spectrum of the parent compound appeared at 6.39, 6.43 and 6.47 microns and were attributed to C-N vibrations in dimers involving cyclic N-H-O, linear N-H-O and N-H-N hydrogen bonds, respectively. All of the bands shifted with dilution to form a strong band at 6.66 microns, close to a 6.68 micron band observed in the present KBr spectra. If the suggested shift in the N-H stretching frequency of the adsorbed polyamides to shorter wave lengths was due to disruption of intramolecular hydrogen bonds, and the frequency assignments of Letaw and Gropp were correct, the dominant 6.45 micron band in the polyamides should be sacrificed on adsorption in favour of the 6.68 band formation. Comparisons among Polyamide A spectra in Figures 2, 4, and 5 indicate a qualitative trend in this direction. The 6.68 micron bands in the adsorbed Polyamide C and E spectra are very weak and do not justify any comment as to contributions of free and hydrogen bonded forms to the N-H bending absorption.

The earlier suggestion, based on analogy, that the 6.53 micron band was a part of the amide II structure had to be changed. Absence of the band in the



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spectra of polyamide films on NaCl and the displacement of the band from the reported structure in monosubstituted amide spectra made the assignment doubtful. The development of the band in KBr and the proximity to the 6.49 micron absorption reported for the ionic form of the carboxyl group in stearic acid adsorbed on the rutile⁸ suggests that adsorbed terminal carboxyl groups in the polyamide chains may be responsible. The observation that the ratios of the 6.53 to 6.45 micron absorbances decrease with increasing polyamide molecular weight supports the tentative assignment.

Conclusions

The results of the present study indicate that the concentrations of polyamides adsorbed on pigments can be determined by analysis of infrared spectra obtained on pressed KBr discs containing known sample weights of recovered pigments. Order of magnitude agreement can be obtained with adsorption determinations based on solution analyses of the depleted polyamide concentrations.

Adsorption of the polyamides induces significant shifts in several bands of the infrared spectra due to dilution, disruption of intra- and intermolecular hydrogen bonds, and interactions with the adsorbent surfaces. Most notable was the apparent loss of the N-H stretching frequency. The probable shift was to a lower wave length which was concealed by interference with the O-H stretching frequency of water adsorbed on KBr. Modification of both amide I and amide II bands by rutile and amide II bands by carbon black indicate that the amide group itself was perturbed by the surfaces.

The spectral data support an earlier hypothesis that the polyamide chains are oriented predominantly with amide groups on the adsorbent surface connected by solvated, looped or coiled hydrocarbon chains.

Acknowledgments

One of the authors (R.H.S.) gratefully acknowledges fellowship grants from the Flint Ink Corporation and the Paint Research Institute. In addition, we are indebted to the National Printing Ink Research Institute for sustained support.

[Received 5 December 1966]

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Discussion at the Scarborough Conference

DR. G. D. PARFITT pointed out that in the stretching region, the water that existed in the KBr could tend to mask any effects in that region. What did Mr. Schaeffer think about water on the surface of rutile; what sort of part did this play in the infrared?

MR. W. D. SCHAEFFER said he assumed Dr. Parfitt was referring to the effects of adsorbed water on the adsorption of both polymer and resulting spectrum. All the pigments had been dried at 110°C before the adsorption experiments were performed; consequently some residual physically adsorbed water remained on the surface and some surface oxide structure may have been perturbed.

The effect of the residual physically adsorbed water on the spectrum of the rutile should be relatively small, since this was a pigmentary grade of rutile. This was not the ideal substance, and as Dr. Parfitt had pointed out in his introductory lecture this was not the ideal grade to use in an infrared study of the surface chemistry of rutile. A much smaller particle size material was necessary, in which the relative number of surface atoms compared to bulk atoms was much increased. When working with pigmentary grades, a minimum response, due to adsorbed water or adsorbed solvent species, would result due to the limited concentration of surface sites. The determination had been carried out under conditions where the system had minimal response to adsorbed water vapour, if indeed much existed on these surfaces.

DR. V. T. CROWL asked whether Dr. Schaeffer had tried the KBr reinforced-disc technique for examining the infra-red spectra of the adsorbed polyamides.

With reinforced discs there was the minimum amount of mechanical disturbance of the specimen and one avoided completely any possibility of interaction with the solvent, e.g. the carbon tetrachloride used to mull the specimen with the KBr.

A second point was concerned with the adsorbance values quoted in Table 6; Polyamide E adsorbed on rutile showed a very low value for the $A_{6.06}/A_{3.43}$ ratio, which was difficult to understand, particularly in connection with the statement in the text that the decrease could not be accounted for by fractionation of the polymer. Could Dr. Schaeffer comment on the interpretation of these adsorbance ratios?

MR. SCHAEFFER replied that initially attempts had been made to introduce adsorbents with adsorbed polyamide into the KBr on the base of the vacuum cell in which he prepared the KBr window. Virtually all the work was done on recovered pigments containing the adsorbed polymers. The pigments were agglomerated since they lost all solvent during the interval between recovery from solution adsorption experiments and introduction into the KBr system. Under these circumstances the scattering by the agglomerated sample was so intense that there was a lack of sensitivity, and it was only after repeated mulling that satisfactory spectra were obtained.

Two techniques had been employed, and the carbon tetrachloride mull was the most satisfactory from the standpoint of the quality of the spectra. From the point of view

of interpretation, he was not sure that carbon tetrachloride was necessarily the most satisfactory technique. The other technique was to redisperse the initial KBr window and then either reform or dilute with more KBr. In this case the spectra did improve but in this additional breaking down of the pellet, the KBr had a chance to adsorb more moisture from the environment. This was the major reason for preferring the carbon tetrachloride mull.

The second question concerned a section of the paper which was omitted in the presentation of the lecture. The most difficult of all of the adsorbance ratios in Table 6 to explain was that of polyamide E on a rutile surface, which was probably the one referred to. The absorbance ratios for the CO stretch to the CH stretch, as well as to the N-H bending to the CH stretch, were perturbed from the standpoint that the absorbance ratios were lower in both cases than for polyamide E in KBr alone, or for the lower molecular weight polyamide A absorbed on rutile.

In the solution adsorption studies of polyamide E on rutile, it was found that the molecular weight distribution was wide enough to give significant preferential adsorption of the higher molecular weight components. At first, the low infrared absorbance ratios for the same samples were attributed to polyamide E fractionation, but if indeed fractionation were involved, the lower molecular weight components should be selectively adsorbed. The volumetric analysis of equilibrated polyamide solutions did not support the point of view.

The remaining explanation possible was a greater perturbation of the amide I and II bands by the adsorption process on rutile for polyamide E than for polyamide A. Why the intensities of the corresponding adsorption bands should be influenced more in the higher molecular weight polyamide was not clear.

Referring back to the work on solution adsorption, it was difficult to say that the polyamide E molecular area on rutile differed greatly, except for the molecular dependence, from polyamide C or polyamide A molecular areas on rutile. Polyamide E shows about the same change, the same response, to the presence of an interface or surface as the other two polymers, so there was no evidence on the basis of molecular areas to support the above suggestion.

DR. W. FUNKE asked why alcohols had been used, as they were poor solvents for polyamide systems. Why were not dimethyl formamide or similar solvents used?

MR. SCHAEFFER felt the point was very well taken, since the present manuscript included only the work with two solvents, *n*-propanol and *n*-butanol. The solution adsorption measurements had included additional solvent systems, mixed solvents incorporating either *n*-decane or water. He had not used dimethyl formamide. Attempts had been made to follow the adsorption behaviour as a function of the quality of the polymer solvation. Since that time chloroform had been used, a solvent which provided as little competition in the spectral region of the polymer as possible.

It was found that the better the solvent, the lower the amount of polyamide adsorbed; a trend comparable to all the published studies on the adsorption of linear polymers.

DR. PARFITT pointed out that the adsorption from solution data were not shown because these were being published elsewhere and had not been published yet. The strong adsorption of the polyamide had been mentioned, and this presumably arose from adsorption isotherms. It had also been suggested, from the experiments, that there was strong interaction with the amide grouping. He asked how the area occupied by the polymer on the surface was related to the molecular weight, and what sort of configuration they adopted at the surface. Would Mr. Schaeffer like to say something about the adsorption isotherms?

MR. SCHAEFFER said this was a fascinating part of the study, and apologised for not having the entire study available. As he had suggested to Dr. Funke the better the solvent system which was employed, the lower effectively was the amount of polyamide

adsorbed. In other words, the adsorption of a given polyamide from two or more solvents could be inversely related to the limiting viscosity number. The higher the limiting viscosity number, the lower was the weight of material adsorbed from solution at the plateau of the typical Langmuirian type isotherm. This applied as long as the solvents were the normal alcohols and mixtures of these alcohols with the hydrocarbons. When water was introduced into the two alcohols, the quality of the solvent became much poorer, and the effective molecular diameter decreased. When the polyamides were adsorbed from these solvent systems on the carbon black surface, the poorer the solvent system, the greater the amount of polyamide which was adsorbed.

When rutile—which could interact very selectively with water—was used as the absorbent, on the other hand, then the presence of water in the solvents had a markedly different effect: it tended to decrease the amount of polymer adsorbed and increase the effective areas of the adsorbed polyamides.

In summary, water in solvents equilibrated with rutile influenced the interaction of polyamides with specific surface sites; in the case of carbon black, the water influenced the polyamide configuration by limiting the solvation. Latter systems were surprising, because the Elf-5 surface contained about 3 per cent chemisorbed oxygen, and might be expected to interact selectively with polar groups on the polyamide and water.

DR. PARFITT felt that it was a question of energy of interaction of water with the surface. An oxide surface apparently dried at 120 C would normally absorb water rapidly on exposing it to the atmosphere.

Reviews

SURFACE TENSION AND ADSORPTION

By R. DEFAY and I. PRIGOGINE, with the collaboration of A. BELLEMANS (translated from the French by D. H. EVERETT). Longmans, Green & Co. Ltd., London, 1966. Pp. xxxii+432. Price 100s.

For many of the readers of this *Journal* surface chemistry is a prime interest, hence the title of this book will attract their attention. Those with more than a passing interest in thermodynamics will recognise the names of the authors and expect on closer examination to find an authoritative account of the thermodynamics of interfaces. They will not be disappointed except, perhaps, in the fact that not all interfaces are considered. The major proportion of the 21 chapters deals with the thermodynamics of liquid surfaces. Some consideration is given to the surface tension of solids with particular reference to nucleation phenomena, but adsorption by solids receives little attention; mention is made of adsorption from the vapour phase, but there is no discussion of that from solution by solids.

In his classical work Gibbs laid the foundation of the thermodynamics of interfaces. The authors of this volume present an authoritative exposition based mainly on the Gibbsian treatment. The first five chapters contain the definitions and the development of the thermodynamic formulae for interfacial systems. A detailed investigation of the Gibbs adsorption equation is then given and followed by several chapters on the surface tension (static and dynamic) of pure liquids and solutions, and a brief discussion of the properties of insoluble films. The Gibbs model is replaced for solutions by a statistical approach based on the assumption that a monolayer of given composition separates the two bulk phases. The shortcomings of this model are discussed and a treatment involving a multiple layer model is developed which is then compared with that using the Gibbs approach. The important effects of surface curvature are then considered and lead to an examination of the concept of surface tension of a solid surface, from which the thermodynamic aspects of nucleation are developed and reviewed. The final chapter deals with adsorption of electrolytes and electrocapillarity.

Although there is liberal reference to experimental work, the book contains mainly a mathematical treatment which in parts is quite formidable, but nevertheless readable. Production, style and translation are all excellent; the price is very reasonable. For those who wish to study the subject in depth this book will be an asset. Herein lie the fundamentals ready to be exploited.

G. D. PARFITT.

RUBBER : NATURAL AND SYNTHETIC, 2ND EDITION

By H. J. STERN. Maclaren & Sons Ltd., London. Pp. 518. Price £5 5s.

The first edition of this book appeared in 1954, so that a revised edition was due and is very welcome. The arrangement of the new edition is somewhat different from that of its forerunner. The book is no longer divided into two parts (natural, synthetic), and, for example, the first treatment of synthetic rubber comes in Chapter 3 instead of Chapter 8 as previously.

The chapter headings, as follows (approximately), indicate the coverage: (1) historical, plantation rubber, (2) raw rubber, properties, etc., (3) synthetic rubber, emulsion polymers, (4) butyl and ethylene, etc., copolymers, (5) stereoregular rubbers, thermoplastics, (6) vulcanisation, antioxidants, (7) compounding ingredients, (8) rubber machinery, (9) manufacturing processes, (10) latex technology, (11) properties of rubber. Thus 11 chapters replace the previous 13.

To write a book covering a particular field of technology completely is a formidable task nowadays, and Dr. Stern is to be congratulated not only in doing just this but also in filling a serious gap in the technological literature. It is difficult to think of any other book which could be recommended to anyone wanting an up-to-date general treatise on the whole subject of rubber technology.

The most serious criticism that can be levelled against the book is the divergence into the realm of plastics in various places, which seems hardly justified in a book of this title, especially since, as mentioned, rubber technology would seem to be a big enough subject in itself. The author explains that accounts of certain plastics, e.g. polyvinylchloride (cf. p. 210), are included because they have some rubberlike properties, but this ignores the essential differences between elastomers and thermoplastics. Again what rubbery properties does ptfе, for example, have to justify its inclusion in *Rubber: Natural and Synthetic*? On the other hand an important material used in tyre manufacture, insoluble sulphur, finds no mention.

The book seems to contain more printing errors than the first edition. Some noted were:

p. 29, for the reference 24 read 23.

p. 208, Fig. 5.8, for "from" read "foam."

p. 467, Fig. 11.4, line 6, for "molecular" read "molecule."

p. 507, for "frequency" read "frequently."

On the other hand the reader has gained something in the reduced weight of this second edition, thus:

Weight of book, 1st edition—3 lb 7 oz

„ „ „ 2nd edition—2 lb 11 oz

As mentioned in the review of the first edition (*JOCCA*, January 1955, p. 48), the choice of a comparatively thick "art" paper appears to be responsible for these comparatively high figures.

Finally the book can be recommended to members of the Association who want a general treatise on rubber technology (but which does not deal at any great length with the use of elastomers in coatings).

W. H. STEVENS.

Information Received

(In case of difficulty regarding addresses, members and subscribers to the JOURNAL should apply for details to the General Secretary of the Association at the address shown on the front cover.)

A new booklet on *Santotherm* heat transfer fluids has recently been published by **Monsanto Chemicals Ltd.** The *Santotherm (FR)* Series I fire-resistant fluids are claimed to operate in a temperature range from -18°C to 315°C , and the Series II fluids to operate in a range from -73°C to 360°C . They are claimed to afford even heating, and to be controllable to within 1°C .

BP Chemicals (UK) Limited, Carshalton Division, have announced that they are to commence manufacture of *Bisol DDSA* (dodeceny succinic anhydride) in commercial quantities. It is claimed that this is the first time that the material has been manufactured in commercial quantities in Britain.

A new speciality addition to the *Cromophthal* range of high performance pigments has been introduced by **Ciba Clayton Ltd.** The new organic pigment, *Cromophthal Red A3B*, is bright bluish red in shade and is claimed to have excellent resistance to heat, light, weathering, solvents and chemicals. It may be used in all high quality pigment applications, but is recommended by the manufacturers for use in strong shade metallic finishes, molybdate chrome blends, or to produce bright bluish reds in pvc and polyolefines.

Also announced by Ciba is *Orasol Red G*, a brilliant red solvent soluble dye recommended for printing inks and lacquers.

Improved production handling and paint performance is claimed by **The Dow Chemical Company** for their new synthetic latex paint additive, *Methocel SA 1214.5*. A cellulose ether, it is said to offer close solubility rate control and good flow and levelling characteristics, particularly in acrylic latex systems.

Greater transfer of ink, superior tone reproduction and improved highlights are advantages claimed for the new *Crosfield Heliostat 260*, the latest development in electrostatically assisted gravure printing from **Crosfield Electronics Ltd.**

The *Heliostat*, which was recently demonstrated jointly by **Crosfield and Fishburn Printing Ink Co. Ltd.**, generates an electrostatic field across the printing nip and draws the ink particles into the pores of the paper, giving optimum ink coverage and eliminating speckling or "dot skip."

The *Heliostat* is a pipe roller, containing a sealed electronic package, which runs in contact with, and is driven by, the impression roller. The surface of the generator roller is covered with conducting rubber, and a high voltage is transmitted to the surface of the impression roller, which is also covered with conducting rubber, producing the required electrostatic action in the printing nip.

Additions to the *Plastokyd* range have recently been announced by **Plastanol Limited**. These are *Plastokyd 300X*, a DCO oil of 27 per cent oil length, *Plastokyd 310XB*, a 30 per cent oil length linseed oil, *Plastokyd 462X*, a 43 per cent linseed oil, *Plastokyd 465X*, a 47 per cent oil length soya/DCO oil, and *Plastokyd 475X*, 40 per cent oil length tall oil fatty acids.

Badische Anilin- and Soda-Fabrik AG have recently added three further pigments to their *Heliogen* range. These are *Heliogen Blue BC*, *Heliogen Green 6GA* and *Heliogen Green 8GA*. The new pigments are claimed to have improved colour strength, cleanness of shade and dispersibility.

A new technical information leaflet, Pigment No. 10, has recently been issued by **Farbwerke Hoechst AG**. The leaflet covers properties and formulation of *PV fast* and *PV* pigments, and *Euviprint D* pigment preparations, for use in printing inks for polyolefines, pvc and aluminium foils. Also announced are two new additions to these ranges, *Permanent Bordeaux HF3R extra power* and *PV Pink FL*.

A new device for accurate temperature control of solids, liquids and gases in the laboratory has been introduced by **GSPK (Electronics) Ltd**. The device, the *Thermonitor*, is simple in operation, requiring only the use of a mercury/glass thermometer. The thermometer is placed in a stainless steel jacket, using mercury as a contact liquid, and one probe of the *Thermonitor* attached to the jacket. The other probe is attached to the thermometer, and after the instrument sensitivity has been adjusted, this probe can be set to the temperature required on the thermometer, after which, it is claimed, this temperature will be maintained to within 2 mm of the thermometer scale for any desired length of time.

Mitchell Craig Pumps Ltd. have recently published a new brochure dealing with their range of side-entering mixers. Reference No. S.E.1, the brochure covers a range of gear- and belt-driven mixers from $\frac{1}{2}$ to 40 hp.

A new quick drying *Parsolac* primer has been introduced by **Sherwood Parsons Ltd.**, a subsidiary of **Donald Macpherson and Co**. The primer is claimed to have improved adhesion, flow and covering power, and incorporate the latest rust-inhibiting pigments.

Continuous level indication of bulk container contents together with up to ten relay control points is available with the *Levelrator*, recently introduced by **Thomas Industrial Automation Limited**. The ten relay control points are infinitely variable along the entire electrode length, and as the instrument is transistorised, it can be mounted, it is claimed, up to one mile from the point of measurement.

Important changes in the activities of **Berk Limited** have been announced. To line up with the policy of concentrating endeavour into the company's more profitable fields, and cutting back central overheads, the Chemicals Division has been divided into two profit-accountable units, responsible separately for manufactured and merchanted products. At the same time the "made to order" plant section of the Engineering Division has been sold to **Pennsalt Ltd.**, a joint company, **BCA Pharmaceuticals**, has been formed with **Cope Allman International Ltd.**, and expansion of the joint sand gravel business with **Ready Mixed Concrete (United Kingdom) Ltd.** is planned.

John & E. Sturge Limited are offering a free sample of emulsion paint containing *Calopake EP* for evaluation by any interested paint manufacturer. *Calopake EP* is one of the Sturge range of precipitated calcium carbonates, claimed to be specifically produced to give increased brightness and opacity in emulsion paint, with improved brushing characteristics, can stability, high wash resistance, and good flow out rating.

Section Proceedings

Thames Valley

Some recent developments in paint testing instruments

The sixth technical meeting of the session was held at the Royal White Hart Hotel, Beaconsfield, on 29 March 1967, when Mr. C. J. H. Monk, of ICI Paints Division, spoke on "Some recent developments in paint testing instruments."

Mr. Monk introduced the subject by outlining the various properties of a paint which it is desirable to measure for specification and other purposes. These properties could be broadly divided into two main groups : (a) Those which could be precisely defined into simple scientific terms, (b) those which were assessed in a subjective manner and could only be defined empirically. The measurement of film thickness, viscosity, gloss, etc., were used to illustrate these groups.

The main requirements for standardising methods of paint testing and the design of paint testing instruments were discussed. The advantages of good testing equipment being available to raw material suppliers, paint manufacturers and customers were pointed out.

Examples of instruments developed by ICI Paints Division were considered in this light and details given of their construction and use.

These were :

- | | | |
|------------------------------------|---|--------------------------------|
| (1) The pressure WPG cup | } | for testing paint in the can. |
| (2) The Cone and Plate Viscometer | | |
| (3) The Gel Tester | | |
| (4) The High Viscosity Rotothinner | | |
| (5) The Mechanical Applicator | } | for paint application testing. |
| (6) The Drying Time Machine | | |
| (7) The Oven Temperature Recorder | | |
| (8) The Pneumatic Hardness Tester | | |

In concluding, the importance of a concise definition of what was to be measured was stressed. Also the advantage of making instruments available which could give results independent of the judgment of the operator was pointed out.

Concerning the future, there was still a need for better paint testing instruments in the fields of measurement not mentioned in the talk. Also there was scope for miniature instruments which the paint technologist could carry in his pocket, and lastly the inevitable automation of paint plant would be largely dependent on the availability of suitable measuring instruments.

The talk was followed by a demonstration of the various instruments discussed. A vote of thanks for a very professional presentation was proposed by the Chairman, Mr. A. G. Holt.

W. S.



20th Technical Exhibition

Applications to exhibit at next year's Technical Exhibition close on 4 September 1967, and a large number of applications have been received, both from the United Kingdom and continental sources. The Exhibition will take place from 25-29 March at Alexandra Palace, London. (The hours of opening were given in the July *Journal*.) Leaflets giving a map and directions in six languages (English, French, German, Italian, Russian and Spanish) have been prepared

for wide distribution on the Continent. It may be possible to supply copies to members wishing to send these to their colleagues and associates abroad, if written application is made to the General Secretary. Similarly, copies of the *Official Guide*, which will be available early next year, may be obtained free of charge by those intending to visit the Exhibition; all members of the Association wherever resident will receive a copy immediately upon publication.

Jordan Award

As announced at the Annual General Meeting, Council has been very pleased to receive from Mrs. L. A. Jordan a bequest for the institution of an Award in memory of her late husband, Dr. L. A. Jordan, who was President of the Association 1947-49, became an Honorary Member in 1955 and presented the first Commemorative Lecture in 1963.

Louis Arnold Jordan, C.B.E., was the Founder Director of the Research Association of British Paint, Colour and Varnish Manufacturers from its inception in 1926 until his retirement in 1959. He died on 1 December 1964 at the age of 72. He had a distinguished academic career at the Royal College of Science and in the 1914-18 war was

concerned with explosives. After the war he held appointments in the chemical industry and for a time was the scientific adviser to the State of Bhopal. As well as his Directorship of the Paint Research Station and Presidency of the Oil and Colour Chemists' Association, he took an active interest in many other bodies connected with the industries and education; he was a member of the Senate of London University and Professor of Chemistry at the Royal Academy of Arts 1958-62. After his retirement he visited India and the Far East on official visits.

It is intended that the first Award of £100, which will be in cash and entirely at the disposal of the recipient, shall be

made at the time of the Association's Jubilee Celebrations in May 1968 and thereafter it is hoped to make the Award biennially.

The Award is open to all members of the Association up to the age of 35 on the final date for the submission of applications which, on this occasion, will be 31 December 1967. There will be two methods of application. First, by direct application in which a paper is submitted of original work which has either been published in the *Journal* or is so submitted for publication. The alternative method would be by recommendation by a superior for work which for reasons of commercial secrecy cannot be published; in this case some form of dissertation would be required from the candidate. It is stressed that all members of the Association wherever resident may apply for the Award and the submission will be judged on scientific and technological content and its merit as a contribution to industry or the Association.

The selection of the recipient for the Award will be made by a Committee under the Chairmanship of the Association's Hon. Research and Development Officer, Mr. A. T. S. Rudram. Appli-

cations are now invited for the first Award and these should be addressed in the first instance to the General Secretary at the address shown on the front cover.



Dr. L. A. Jordan (President 1947-49)

Scottish Section

Student Group

A very pleasant outing to the Covenanters' Inn, Aberfoyle, was held by the Scottish Section, Student Group, on Saturday 24 June. A large number of students and friends enjoyed to the full the hospitality offered at the inn, and

once again the evening was voted an outstanding success.

This is the third year of what has become an annual event, and in view of the popularity it is almost certain that continued success will be forthcoming in the future.

Obituary

Johannes Hoekstra

Many members of the Association who knew Professor Hoekstra, the second President of FATIPEC (1952-53), will be sad to hear of his death on 8 June. He was professor at the Technical University, Delft.

As the second President of FATIPEC he took the chair at the second FATIPEC Congress at Noordwijk, and all who attended the last FATIPEC Congress will remember his contribution on that occasion.

News of Members

Mr. H. T. Skinner, an Ordinary Member attached to the London Section, has been appointed a Director of The Empire Printing Ink Company Limited, a subsidiary of the Ault and Wiborg Group. Mr. Skinner is General Manager of Empire Printing Ink.

Mr. P. F. Sharp, an ordinary member attached to the Bristol Section, recently left British Resin Products Limited, where he was a member of the Surface Coating Technical Service Department, to take up an appointment as Assistant Chief Chemist with Lusteroid Pty, Otahuhu, Auckland, New Zealand.

Colour measurement and colour control

The programme for the course on "Colour measurement and colour control," to be held at South Birmingham Technical College on six successive Thursdays from 19 October to 23 November, has been announced, and is as follows :

19 October.—16.45 : M. H. Wilson and R. W. Brocklebank (Goethean Science Foundation), "The factors which determine how we experience colours." 19.00 : Second part of the introductory lecture.

26 October.—16.45 : Dr. K. H. Ruddock (Imperial College of Science and Technology), "The CIE system of colour measurement." 19.00 : R. W. Brocklebank (Goethean Science Foundation), "The use of colour atlases."

2 November.—16.45 : F. A. Garforth (National Physical Laboratory), "Visual methods of colour measurement." 19.00 : F. Malkin (British Ceramic Research Association), "Colorimeters, their applications and processing of their results by digital computer."

9 November.—16.45 : J. L. R. Landry (Davidson and Hemmendinger Inc.), "Spectrophotometers and their applications." 19.00 : J. L. R. Landry (Davidson and Hemmendinger Inc.), "The use of analogue computers in colour control."

16 November.—16.45 : P. S. Davies (ICI Paints Division), "Colour tolerances." 19.00 : J. M. Adams (The Research Association for the Paper and Board, Printing and Packaging Industries), "The accuracy of colour measurement."

23 November.—16.45 : Miss M. B. Halstead (British Lighting Industries Ltd.), "The effect of lighting on colour rendering." 19.00 : A. J. Ford (Blundell Permoglaze Ltd.), "A method of controlling the formulation and production of paints by computer."

The preliminary programme schedule has been announced for the Annual Meeting of the Federation of Societies for Paint Technology, to be held at Municipal Convention Hall in Minneapolis, Minn., 15-18 October.

The programme is again to be presented on a divisional basis, having three concurrent sessions, A, B and C.

The 32nd Paint Industries Show is also to run concurrently with the Annual Meeting.

IXth FATIPEC Congress

The organisers of the IXth FATIPEC Congress, to be held in Brussels from 12 to 18 May 1968, with the theme "Fundamental aspects of the test methods peculiar to the industry of paints, varnishes, printing inks and related products," have announced that registration for the Congress is now well under way, and, according to the registrations already received, there will be more than five plenary lectures and more than 70 papers.

An exhibition of measuring instruments is also to be held.

Paint industry survey

The Federation of Societies for Paint Technology has engaged David Litter Laboratories to conduct a survey of the paint industry in order to collect information on the latest equipment

being used and the latest development in practices to improve efficiency.

The Federation feels that the combined cost of surface preparation and paint application, which has been calculated to be about 80 per cent of the total cost of the job, might well be reduced substantially, offsetting the cost of the paint used. This would obviously cause a rise in paint consumption.

The Federation hopes that the survey will lead to greater overall knowledge

in the area of efficient and economical production, thereby decreasing overall costs and increasing paint usage.

Anyone with any suggestions or information to offer is invited to contact the following :

Sidney B. Levinson,
Technical Director,
David Litter Laboratories,
116 East 16 Street,
New York, N.Y. 10003.

Register of Members

The following elections to membership have been approved by Council. The Sections to which the new members are attached are given in italics.

Ordinary Members

- FRANCOIS, PETER THOMAS, Chemical Services, PO Box 2, Parklands, Johannesburg, South Africa. (*South African*)
- GRAY, DONALD LEONARD STRANG, B.SC., 14 Rosen Street, Epping, N.S.W., Australia. (*New South Wales*)
- LEONARD, BARRY DAVID, B.SC., International Adhesives & Resin P/L., Sir Thomas Mitchell Road, Chester Hill, N.S.W., Australia. (*New South Wales*)
- MOSS, ARTHUR JAMES, ICI (SA) Ltd., 1 Leyd Street, Braamfontein, Transvaal, South Africa. (*South African*)
- MOSTERT, ALBERTUS IZAK, 37 Launceston Road, New Redruth, Alberton, Transvaal, South Africa. (*South African*)
- MURRAY, COLIN OWEN, 12 Carlisle Crescent, Durban North, South Africa. (*South African*)
- RANKIN, JOHN, B.SC., 10 Andy Street, Guildford, Sydney, N.S.W., Australia. (*New South Wales*)
- ROLFE, AUSTIN PARMA, B.SC., Fabco Products, 150 Wigram Road, Glebe, N.S.W., Australia. (*New South Wales*)
- ROUSE, ROBERT EARNSHAW, B.SC., 27 St. Michael Road, New Redruth, Transvaal, South Africa. (*South African*)
- SOUTER, THOMAS GEORGE, B.SC., A.S.T.C., 55 Lucas Road, East Hills, Sydney, N.S.W., Australia. (*New South Wales*)
- TAYLOR, COLIN JAMES, A.R.I.C., Van Leer Packaging, R & D Div., PO Box 32, Mobeni, South Africa. (*South African*)
- WISHART, ARTHUR DENNISON, c/o British Paints (Aust.) Pty. Ltd., Gow Street, Bankstown, N.S.W., Australia. (*New South Wales*)

Associate Members

- BARNES, ASHLEY LEWIS, c/o BASF, Aust. Ltd., 11b Lachlan Street, Waterloo, N.S.W., Australia. (*New South Wales*)
- BOOTH, MICHAEL D'ABROU, c/o Baker Perkins Pty. Ltd., 4 Atchison Street, Crows Nest, N.S.W., Australia. (*New South Wales*)
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- McLOUGHLIN, JOHN ANTHONY, A. C. Hatrick Pty, Ltd., 49-61 Stephen Road, Botany, N.S.W., Australia. (*New South Wales*)

Junior Members

CRAIG, KENNETH JOHN, 11 Burton Avenue, Parkholme, South Australia.

(*South Australian*)

PURNELL, STEPHEN JOHN, Taubmans (WA) Pty. Ltd., Hamilton Street, Queens Park, Western Australia.

(*West Australian*)

Forthcoming Events

Details are given of meetings in the United Kingdom up to the end of the month following publication, and in South Africa and the Commonwealth up to the end of the second month.

Tuesday 12 September

West Riding Section. Symposium on "Current Trends in Paint Additives," to be held at Bodington Hall, University of Leeds, Otley Road, at 7.30 p.m. Full details of the programme were given in the August issue of the Journal.

Dr. R. Piper, "Fire Prevention in the Paint Industry," by Dr. H. D. Taylor, to be held at Chamber of Commerce House, Birmingham, 15, at 6.30 p.m.

Manchester Section. Works Visit to Dutton's & Thwaites' Breweries, Blackburn.

Wednesday 13 September

Manchester Section. Junior Lecture: "Corrosion and Paint," by Mr. H. F. Clay (Cromford Colour Co. Ltd.), at the Manchester Literary & Philosophical Society, 36 George Street, Manchester, 1, at 4.00 p.m.

Thursday 28 September

Midland Section—Trent Valley Branch. "Dispersible Pigments," by Dr. F. M. Smith (Geigy UK Ltd.), to be held at the British Rail School of Transport, London Road, Derby, at 7.30 p.m.

Thames Valley Section. "Interfacial Phenomena in Printing," by Mr. K. Pond, to be held at Royal White Hart Hotel, Beaconsfield, Bucks, at 7.00 p.m.

Friday 15 September

Midland Section. Annual Ladies' Evening, to be held at Westbourne Suite, Botanical Gardens, Birmingham, 15, at 7.00 p.m.

Friday 29 September

Irish Section. "Quality Control of Organic Pigments," by Dr. J. D. Saunders, to be held at the Clarence Hotel, Wellington Quay, Dublin, at 8.00 p.m.

Bristol Section. Chairman's Address by Mr. D. S. Newton.

Saturday 16 September

Scottish Section—Student Group. "Primers," by Mr. G. Scott (Federated Paints), to be held at Lorne Hotel, Sauchiehall Street, Glasgow, at 10.00 a.m.

Wednesday 20 September

London Section. Chairman's Evening. "Art Forms from Newer Materials" by R. N. Wheeler, to be held at the New Engineering Block, University College, London, W.C.1, at 6.30 p.m.

Monday 2 October

Hull Section. A talk by Mr. P. J. Gay, title to be announced later, to be held at the Hull College of Technology, at 7.00 p.m.

Friday 22 September

Midland Section. "Safety in the Paint Industry,"—"Storage and Handling," by Mr. F. Tennant, "Toxicity," by

Thursday 5 October

Newcastle Section. "Coil Coating," by Mr. D. S. Newton, to be held at the Royal Turks Head Hotel, Grey Street, Newcastle upon Tyne, at 6.30 p.m.

Monday 9 October

London Section—Southern Branch. Film Evening presented by Hoechst (UK) Ltd., to be held at the Keppel's Head Hotel, The Hard, Portsmouth, at 7.30 p.m.

Tuesday 10 October

West Riding Section. "The Work and Activities of the Paint Research Station," by Dr. S. H. Bell, to be held at the Griffin Hotel, Boar Lane, Leeds, 1, at 7.30 p.m.

Thursday 12 October

Scottish Section. "Painting the Q4," by Mr. A. Pisacane (John S. Craig & Co. Ltd.), to be held at the Lorne Hotel, Sauchiehall Street, Glasgow, at 6.00 p.m.

Friday 13 October

Manchester Section. "Towards Automation," by Mr. H. R. Touchin, at the Manchester Literary & Philosophical Society, 36 George Street, Manchester, 1, at 6.30 p.m.

Hull Section. 24th Annual Dinner and Dance at the Hotel Eden, Willerby.

Saturday 14 October

Scottish Section—Student Group. "Explosives and the North Sea Search," by Mr. J. E. Dolan (ICI Ltd.), to be held at the Lorne Hotel, Sauchiehall Street, Glasgow, at 10.00 a.m.

Wednesday 18 October

London Section. "Irradiation Curing of Paint Films," by Dr. F. L. Dalton, at New Engineering Block, University College, London, W.C.1, at 6.30 p.m.

Friday 20 October

Midland Section. "Law of Contracts of Employment," by Mr. D. Mather, to be held at Chamber of Commerce House, Birmingham, 15, at 6.30 p.m.

Manchester Section. Annual Dinner and Dance at the Piccadilly Plaza Hotel.

Wednesday 25 October

Scottish Section—Eastern Branch. "Carbon Blacks," by Mr. Mynett (Columbia International), to be held at the Wee Windaes Restaurant, High Street, Edinburgh, at 7.30 p.m.

Friday 27 October

Irish Section. "The Measurement of Colour by Instrumentation," by Mr. P. V. Foote—Introduction by Dr. S. H. Bell, to be held in the Imperial Hotel, Cork, preceded by a works visit to Michelstown Creameries at 3.00 p.m.

Bristol Section. "Methods of Paint Application," by Mr. A. A. B. Harvey (Institute of Metal Finishing), to be held at the Royal Hotel, Bristol, at 7.15 p.m.

Tuesday 31 October

Thames Valley Section. Practical Contributions to the Analysis of Paints," by Mr. E. L. Deeley, to be held at the Royal White Hart Hotel, Beaconsfield, Bucks, at 7.00 p.m.

Errata

In the list of Section Officers and Committees in the August issue, it is regretted that Mr. G. H. Hutchinson's name was erroneously shown as Scottish Section, Eastern Branch Representative on Council. Branches do not have a representative on Council. Mr. Hutchinson is an Elective Member of Council, and represents the Eastern Branch on the Scottish Section Committee.

Also in error: Scottish Section, line 11, Craiglaw not Graiglaw; line 13, P. Birrell not B. Birrell; line 14, Kilgraston not Kilgarston. Eastern Branch, line 4, Inverleith not Inverleity; line 13, Comiston not Commiston; line 22, A. B. Fleming not A. R. Fleming.

Oil and Colour Chemists' Association

President: F. SOWERBUTTS, B.SC.TECH.

The Oil and Colour Chemists' Association was formed in 1918, to cover paint, printing inks, pigments, varnishes, drying and essential oils, resins, lacquers, soaps, linoleum and treated fabrics, and the plant, apparatus and raw materials useful in their manufacture. In 1923 it absorbed the Paint and Varnish Society. The stated purpose of the Association is to promote by discussion and scientific investigation the technology of the industries concerned with the above-mentioned products, and to afford members opportunity for the interchange of ideas. This is achieved by the regular holding of ordinary meetings at which papers are presented, and the organisation of annual technical exhibitions, biennial conferences, educational activities and practical co-operative experimental work. Details of these activities are given in the *Journal of the Oil and Colour Chemists' Association*, which is published monthly, and whose pages are open to receive communications and other pronouncements on scientific and technical matters affecting the members of the Association and the industries concerned. The Association's meetings also afford opportunities for members to meet informally and socially.

There are Sections of OCCA in Auckland, Bristol, Hull, Ireland, London, Manchester, the Midlands (with a Trent Valley Branch), Newcastle upon Tyne, New South Wales, Queensland, Scotland (with an Eastern Branch), South Africa (with Branches in the Cape, Transvaal and Natal), South Australia, Thames Valley, Victoria, Wellington, West Australia and the West Riding, and these are responsible for the conduct of their own local affairs. There is also a General Overseas Section. There is also a close alliance between the Association, the Federation of Societies for Paint Technology in the United States, and the Fédération d'Associations des Techniciens de l'Industrie des Peintures, Vernis, Emaux et Encre d'Imprimerie de l'Europe Continentale (FATIPEC). The Association also maintains cordial relations with the Scandinavian Federation of Paint and Varnish Technicians (SLF).

Ordinary Membership is granted to scientifically trained persons, and Associate Membership to others interested in the industries covered. Junior Membership, which is intended primarily for students, is open without restriction to persons under the age of 21 and to those up to 25 who are following a course of technical study. The annual subscription in each case is three guineas, except for Junior Members whose subscription is 10s. 6d. An entrance fee of 10s. is payable by all members. Applications for membership are invited from suitably qualified persons who are engaged or otherwise interested in the industries noted above. Applications, which should be supported by two members of the Association (one of whom must be an Ordinary Member), should be forwarded to the General Secretary at the address given below. Application forms and full details of membership may be obtained from the offices of the Association.

PUBLICATIONS

Journal of the Oil and Colour Chemists' Association. Published monthly. Subscription rate to non-members in UK and abroad, £7 10s. p.a. post free; payable in advance.

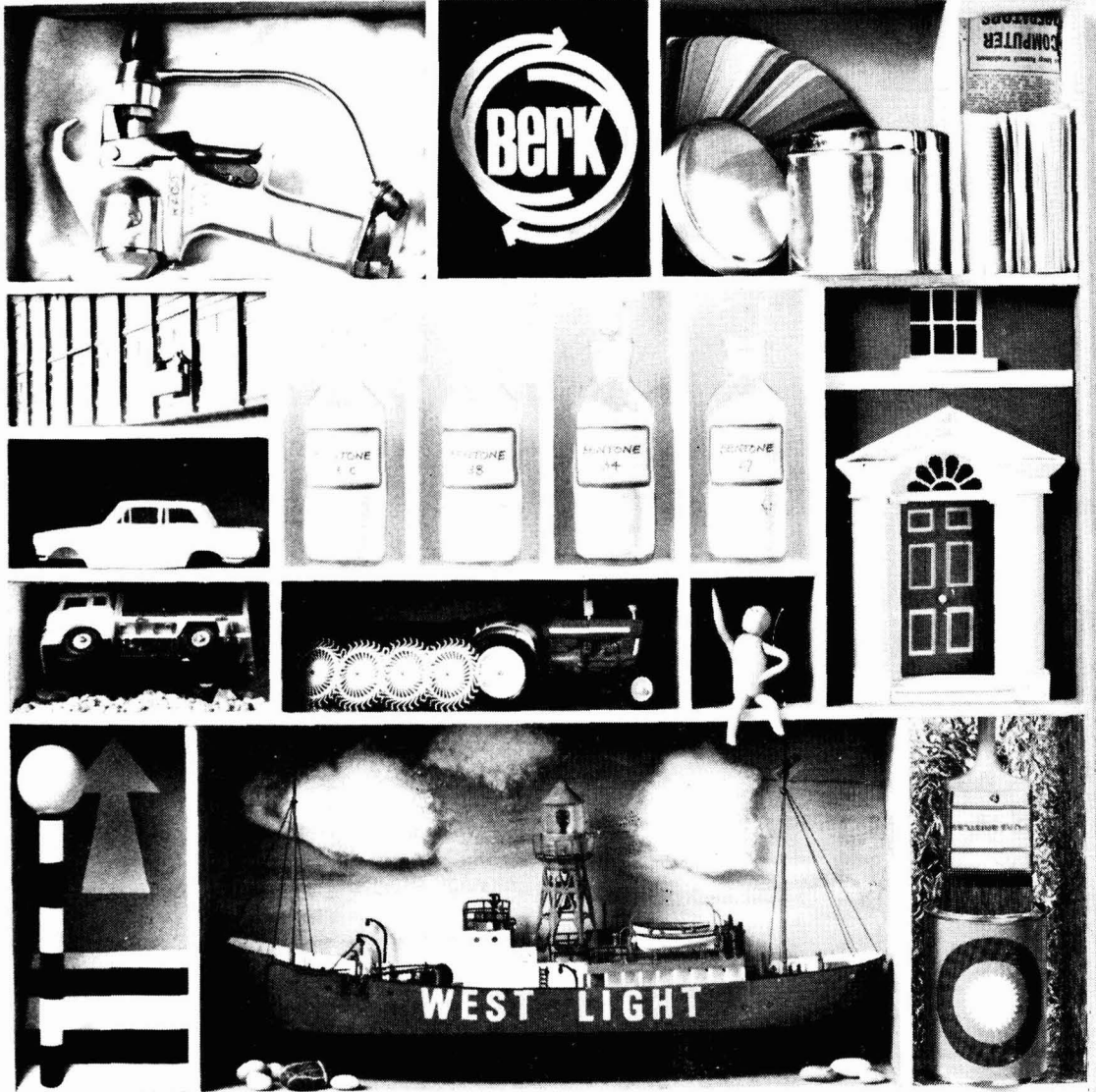
An Introduction to Paint Technology (Second Edition). Pp. 187, illustrated, with index, 15s. (including postage).

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- Part 1 : " Non-convertible Coatings," Pp. 326, 35s.
- Part 2 : " Solvents, Oils, Resins and Driers," Pp. 239, 35s.
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- Part 4 : " The Application of Surface Coatings," Pp. 345, 35s.
- Part 5 : " The Testing of Paints," Pp. 196, 35s.
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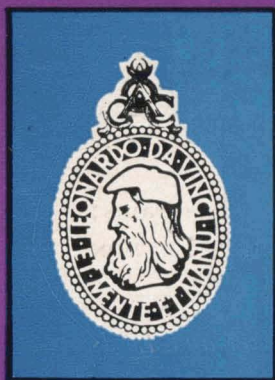
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