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Journal of the Society of Cosmetic Chemists

Contents

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i

INDEX TO ADVERTISERS

A new force enters the field of perfumery. On July 1, 1966, **Bush Boake Allen Ltd** will commence operations. This development follows the amalgamation of three well known suppliers to the perfumery and cosmetics industries: W. J. Bush & Co. Ltd, A. Boake, Roberts & Co. Ltd and Stafford Allen & Sons Ltd. From July 1 these companies will cease trading as separate organisations and will merge their activities into one major entity, which will operate as a member company of the Albright & Wilson Group. As a result, Bush Boake Allen Ltd will be able to provide a comprehensive service which will be one of the finest of its kind. Moreover, with the pooled resources of Bush Boake Allen Ltd, customers will benefit from the vast store of consolidated knowledge and technical facilities. Equally important, there will be available a wider and more versatile range of products than has previously been obtainable from a single source. With the formation of **Bush Boake Allen Ltd** all customers are assured of an improved and uninterrupted service, and of the continued availability of products formerly supplied by the constituent companies. A brochure will shortly be circulated which will give fuller information about this important amalgamation. As a single company making a range of products for the perfumery and cosmetics industries, **Bush Boake Allen Ltd** will set new standards of quality, research and service. Enquiries should be addressed to: Bush Boake Allen Ltd Perfumery Division, Blackhorse Lane Walthamstow, London E.17 Telephone: LARkswood 5454

Bush Boake Allen

Food and Cosmetics Toxicology

Editor : L. Golberg
Assistant Editor : A. J. Cohen

This outstanding journal, published for the British Industrial Biological Research Association, will be of great value and interest to those scientists who need to be fully informed of the current trends in food and cosmetics toxicology. The subject is discussed under the following headings :

Research Section : contains original research articles that will keep toxicologists and other scientists abreast of the most recent advances in the field.

Review Section : provides information on papers dealing with the biochemical, pharmacological, toxicological, medical and veterinary aspects of the subject.

Information Section : divided into the following sub-headings—Legislation : deals with world changes in legislation relating to food additives and contaminants, cosmetic and toilet preparations, etc.
Articles of General Interest :—discussions of more general topics and of papers appearing in other journals reflecting progress and opinion in toxicology.
Toxicology : Abstracts and Comments :—These are more than mere digests of papers published throughout the world ; they are invariably more lengthy than orthodox abstracts, containing all the salient facts to be found in the original article plus the comments of the Editor and his colleagues.

Summary of Toxicological Data

Letters to the Editor   Book Reviews   Forthcoming Papers

Natural Tocopherols in growing use as anti-oxidants
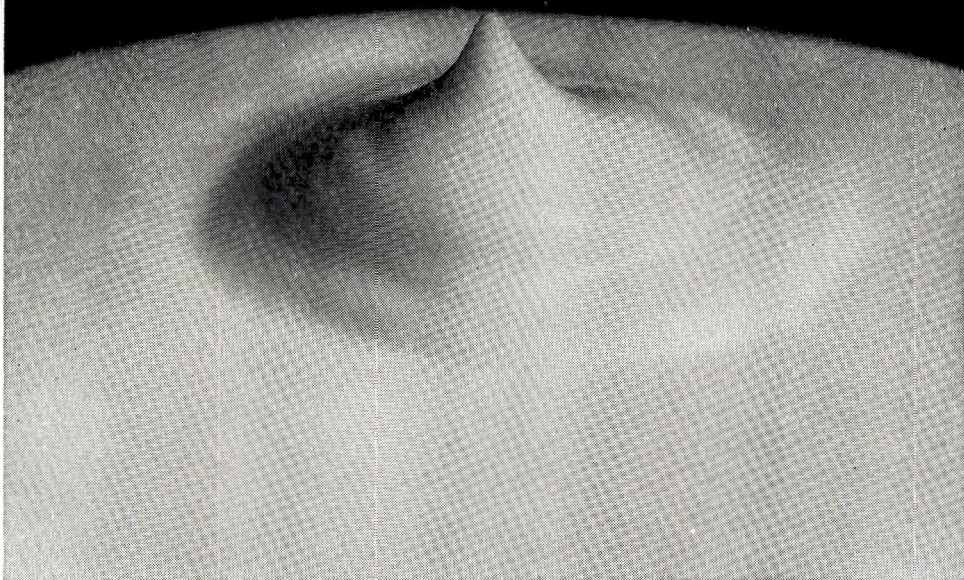
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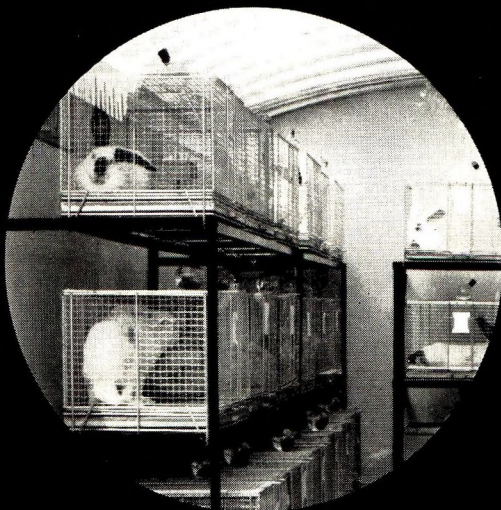TALANTA was established as a medium for the rapid publication of papers dealing with all aspects of analytical chemistry. As an international journal, contributions are expected to be of a very high standard and to make definite contributions to the subject. Papers submitted for publication must be new publications. They may be written in English, French or German. Special importance is attached to work dealing with the principles of analytical chemistry in which the experimental material is critically evaluated, and to similar fundamental studies. Reviews in rapidly expanding fields, and reviews of hitherto widely scattered material, are considered for publication, but should be critical. Original papers, short communications and reviews are refereed. Preliminary communications are refereed urgently and accorded priority in publication. Correspondence of interest to analytical chemists is welcomed by the Editor-in-Chief at whose discretion it is published.
Monthly

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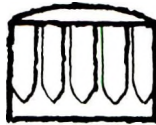
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SYNOPSES FOR CARD INDEXES

The following synopses can be cut out and mounted on 5″ × 3″ index cards for reference without mutilating the pages of the Journal.

Techniques for assessing the rheological properties of toiletry and cosmetic products: P. SHERMAN. *Journal of the Society of Cosmetic Chemists* **17** 439-465 (1966)

Synopsis—Techniques for assessing textural properties of materials ranging from liquids through semi-solids to solids are considered. Methods described in some detail, and reviewed critically, are viscometry at low and high rates of shear for liquids and semi-solids, penetrometers and cohesion for semi-solids, and shear or compression between parallel plates and modulus of rigidity for solids. Choice of method for a particular consistency depends on whether information is required on sample structure or on its performance under normal usage conditions. In the latter case slow deformation should be used when measuring firmness, and rapid deformation when measuring ease of spreadability.

Thin-layer chromatographic techniques in residue analysis: J. THOMSON and D. C. ABBOTT. *Journal of the Society of Cosmetic Chemists* **17** 467-492 (1966)

Synopsis—Thin-layer chromatography has rapidly developed into a precise technique of considerable use to the residue analyst. This paper attempts to deal succinctly with all aspects of thin-layer chromatography, from the choice of the adsorbent to the final documentation of the developed plate. Recent advances in thin-layer chromatography, wedge-layer, multi-band layer and gradient-layer chromatography are also covered by the paper.

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Techniques for assessing the rheological properties of toiletry and cosmetic products

P. SHERMAN*

Presented at the Symposium on "Physical Methods," organised by the Society of Cosmetic Chemists of Great Britain, in Bristol on 17th November 1965.

Synopsis—Techniques for assessing textural properties of materials ranging from liquids through semi-solids to solids are considered.   Methods described in some detail, and reviewed critically, are viscometry at low and high rates of shear for liquids and semi-solids, penetro-meters and cohesion for semi-solids, and shear or compression between parallel plates and modulus of rigidity for solids.   Choice of method for a particular consistency depends on whether information is required on sample structure or on its performance under normal usage conditions.   In the latter case slow deformation should be used when measuring firmness, and rapid deformation when measuring ease of spreadability.

INTRODUCTION

Consistency limits for cosmetic products range from the solid state at one end of the scale, to the fluid state at the other end.   Rheology is usually defined as the science of deformation and flow, so that in order to study the rheological properties of cosmetics it is necessary to select methods which will measure these attributes over a wide range of con-sistencies.   Many of the methods to be described have been in use for some time, while others have been introduced recently.   A high proportion of these methods is used on products other than cosmetics, but of similar consistency, so that there is no reason why they should not be applied **to** testing the latter.

When selecting a suitable method for rheological examination of any material the following points should be considered.

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*Unilever Research Laboratory, Welwyn, Herts.

(a) Should the test provide information about the static structure of the product, i.e. under conditions involving only slight structural change?

(b) Should the test conform to practical usage conditions, i.e. conditions which often involve more than slight structural breakdown?

(c) Do we require an empirical method which merely simulates the mechanical action involved when the product is used?

Under (a) and (b) behaviour is defined in terms of physical values which have mathematical significance, whereas under (c) arbitrary values are derived which cannot easily be inter-related with one another. Discussion will be restricted to (a) and (b) since each method falling into category (c) is specific for a single process.

Tests which cause little alteration in sample structure are usually time consuming, so that they are not suitable for routine control purpose. They should be restricted to fundamental study of structure. Category (b) tests are more readily applied to routine examination, since many tests can be made daily without difficulty. If the maximum value is to be derived from the latter test, however, the test conditions should be such that the product is sheared to approximately the same extent as when used. These conditions cannot usually be estimated accurately.

Table I

Consistency	Test Methods	
	Quantitative	Qualitative
Fluid	Viscometry (*Table II*)	
Semi-solid	Viscometry (*Table II*) Forces of cohesion Modulus of rigidity	Penetrometers – rod, cone, sphere

Solid	Parallel plate viscoelastometer
	  (Creep behaviour under
	  constant stress)
	Compression between parallel
	  plates
	Torsion of hollow cylinder
	Torsional vibration of solid
	  cylinder
	Resonance techniques
	Weissenberg rheogoniometer;
	  sample response to stress
	  varying with time
		Penetrometers – rod, cone, sphere
		
		Sectilometer
		
		Indentation by falling sphere
		N.I.R.D. – B.F.M.R.A. extruder

For ease of discussion consistencies will be classified as fluid, semi-solid, or solid, although there is obviously no sharp demarcation between them. Methods used to examine these three types of consistency are summarized in *Table I*. It is immediately apparent that one technique can often be

used to examine more than one type of consistency. Some of these techniques which require the least complicated apparatus, and which find general use, will be described in some detail.

VISCOMETERS

Theory

No force is required to bring about deformation of materials which show true fluid (Newtonian) flow. They have a constant viscosity irrespective of the applied force.

Newtonian flow can be explained as follows. Let the space (x) between two parallel planes A (upper) and B (lower) be filled with fluid (*Fig. 1*). When a force F is applied to A it moves at a constant velocity (u) if B is stationary. As a result, all the liquid between A and B does not move with identical velocity; instead the velocity varies from u in the layer adjoining A to O in the layer adjoining B. The rate of change in fluid velocity with distance from A, or rate of shear v, is given by du/dx. Shearing stress (S) is the force applied to unit area A. The viscosity of the liquid (η) is given by S/v. Since v always changes to the same extent per unit change in S, it follows that η remains constant, and that it can be determined by a single measurement with any viscometer.
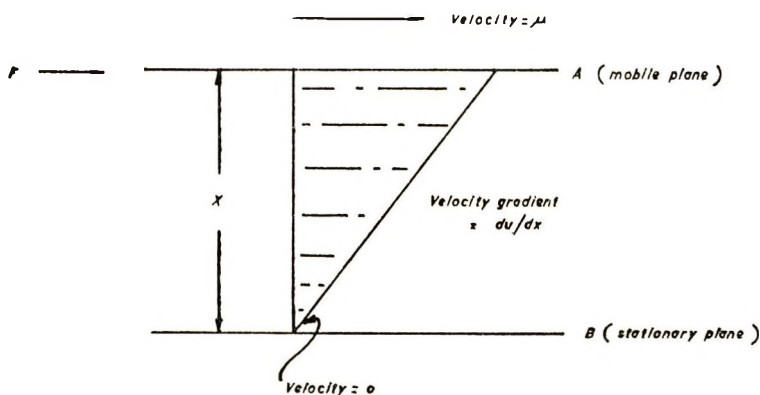
Figure 1 Model to illustrate Newtonian Flow

Many suspensions, emulsions, etc., show more complex (non-Newtonian) behaviour. In some cases the increase in v grows progressively larger per unit increase in S, up to a limiting value of S, so that η decreases. Above the critical value of S the ratio S/v, and therefore η, remains constant.

This type of behaviour is exhibited when structure is broken down during shear. Materials within this category which flow as soon as stress is applied are called pseudoplastics, whereas those requiring a minimum shearing stress (S_o) to establish flow are called plastics (*Fig. 2*).
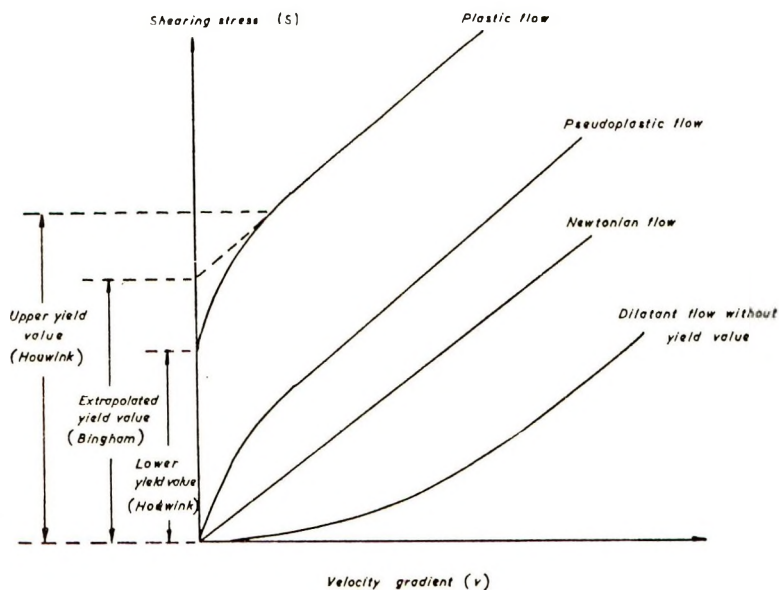
Figure 2   Types of flow behaviour

In dilatant flow v decreases as S increases, so that η increases. This behaviour represents the reverse of pseudoplastic flow if there is no yield value, and the reverse of plastic flow if a yield value is observed. Most powders and closely packed dispersions exhibit dilatancy when closely packed. When sheared the packing must become looser, i.e. there is an initial increase in volume, before the individual particles can move past one another (1).

Two other stress values may be quoted when reporting plastic flow data (2). These are the extrapolated yield value, which is the intercept on the S axis obtained by extrapolating the linear portion of the S – v curve, and the upper yield value, which refers to the value of S at which linear flow is first established (*Fig. 2*).

Pure fluids never show a true yield value. It is often found in concentrated dispersions of liquid droplets, or solid particles, in fluid media. To establish that a yield value actually exists it is necessary to establish

the S – v relationship down to low values of v, and *not* by extrapolating the linear part of what may actually be a pseudoplastic curve.

Since the viscosities of pseudoplastic, plastic, and dilatant systems vary with v, measurements taken at a single value of v have little significance. Especially when comparing the flow behaviour of two different systems η should be measured over a wide range of v. Because system 1 has a larger η than system B at one value of v it does not necessarily follow that this order will apply at another v. "Single point" determinations in this case can lead to incorrect conclusions.

A critical comparison

Commercial instruments of many designs are available for viscosity measurements. *Table II* classifies some of those in general use according

<div align="center">Table II</div>

Viscometer	Suitability for measuring .	
	Newtonian Flow	Non-Newtonian Flow
1. Coaxial cylinder viscometers		
Stormer	✓	✓
Portable Ferranti	✓	✓
Epprecht Rheomat	✓	✓
Haake Rotovisko	✓	✓
Brookfield	✓	✓
Merrill-Brookfield High Shear	✓	✓
Weissenberg Rheogoniometer (Farol Research Engineers, Bognor)	✓	✓
2. Capillary viscometers		
Glass U-tube (a) Single bulb	✓	
(b) Multi	✓	✓
Redwood	✓	
Variable pressure plastometer	✓	✓
Techne vibrating piston	✓	✓
Instrom capillary rheometer	✓	✓
3. Cone-Plate viscometers		
Ferranti	✓	✓
Weissenberg Rheogoniometer	✓	✓
Haake Rotovisko	✓	✓
4. Falling and rolling sphere viscometers		
Höppler	✓	
5. Ultrasonic viscometer		
Ultraviscoson	✓	

to the principles involved in their operation. The equations involved in calculating η from the acquired data are given in *Table III*.

Most types of viscometer, excepting the falling sphere and ultrasonic viscometers, will measure both Newtonian and non-Newtonian flow properties. The cone-plate viscometer is the only one which, with a small

Table III

	CAPILLARY	COAXIAL CYLINDER	CONE-PLATE	FALLING SPHERE
VISCOMETER				
NEWTONIAN VISCOSITY η	$\eta = \pi P R^4/8LV$	$\eta = \dfrac{G\left(\frac{1}{R_1^2}-\frac{1}{R_2^2}\right)}{4\pi h\,\Omega}$	$\eta = \dfrac{3G}{2\pi R^3}\Big/\dfrac{\Omega}{\psi}$	$\eta = \dfrac{2}{9}\left(\dfrac{d_1-d_2}{v}\right)g\,R^2$ UNCORRECTED
NON-NEWTONIAN VISCOSITY η_∞	$\eta_\infty = \dfrac{\pi R^3 g\sigma}{8LR}\cdot\dfrac{1}{\left(\frac{dQ}{dP}+\frac{P}{4}\cdot\frac{d^2Q}{dP^2}\right)}$	$\eta_\infty = \dfrac{M}{4h\Omega}\left(\dfrac{1}{R_1^2}-\dfrac{1}{R_2^2}\right)-\dfrac{v}{\Omega}\ln\dfrac{R_2}{R_1}$		
RATE OF SHEAR v	$v_{capillary\ wall}=\dfrac{4Q}{\pi R^3}$ $v_{axis}=0$	$v_{max}=\dfrac{2\Omega}{R_1^2\left(\frac{1}{R_1^2}-\frac{1}{R_2^2}\right)}$ $v_{min}=\dfrac{2\Omega}{R_2^2\left(\frac{1}{R_1^2}-\frac{1}{R_2^2}\right)}$	$v=\dfrac{\Omega}{\psi}$	$v_{max}=\dfrac{3V}{2R}$ $(\theta=90°)$ $v_{min}=0$ $(\theta=0°)$
SHEAR STRESS S	$\dfrac{PR}{2L}$	$\dfrac{\left(\frac{1}{R_1^2}-\frac{1}{R_2^2}\right)}{4\pi h}$	$\dfrac{3G}{2\pi R^3}$	
YIELD VALUE f	$\dfrac{P_0\,g\sigma R}{2L}$ $P_0=P_{v\sim0}$	$\dfrac{S\cdot G_1}{\ln(R_2/R_1)}$	SG_1	

G_1 = EXTRAPOLATED VALUE OF TORQUE FOR $\Omega=0$
σ = DENSITY OF MERCURY
h = CONSTANT FOR CONVERTING FLOWMETER READINGS INTO CCS/SEC. EFFLUX

cone angle, provides uniform shearing conditions throughout the whole of the sample. In a capillary viscometer v varies from O at the capillary axis to a maximum at the capillary wall surface. Viscosity measurements in a coaxial cylinder viscometer involve rotation of one of the cylinders. If the outer cylinder is rotated then the torque transmitted to the inner cylinder is measured. In this case v varies from a maximum at the rotating cylinder surface to a minimum at the inner cylinder surface, but by suitable design, so that the gap between the two cylinders is small, this shear gradient is minimized. When the outer cylinder remains stationary and the inner cylinder rotates, e.g. Haake "Rotovisko," η is calculated from the viscous drag exerted on the latter by the sample.

Capillary viscometers cannot be used to study the effect of time of shear at any v on η since the sample in the capillary is continuously changing. As will be shown later, such information can be of value when elucidating the structure of concentrated dispersions. On the other hand, this deficiency can be advantageous when dealing with systems showing time-dependent structure breakdown and recovery if one is interested in

only the instantaneous η prior to structure alteration.   When interpreting data obtained with a capillary viscometer, corrections must be made for the following phenomena.

(a) When the test sample passes from the wider tube, in which it is held initially, into the very much narrower diameter capillary, the sample is deformed around the shoulders of the wider tube. The correction which must be applied for this "end effect" (or more correctly, the "entrance effect") is minimized when the capillary has suitable dimensions, e.g. a length/radius ratio of 200/1. The effect is then insignificant compared with the pressure drop due to flow in the capillary.

(b) Entry of a disperse system into the narrow capillary can lead to axial migration of the dispersed phase. This results in concentration fluctuations across the capillary, the principal reduction in concentration occurring in the sample layers adjacent to the capillary wall.

(c) Not all the applied pressure is used to shear the sample. Some is used to impart kinetic energy to the sample when it enters the capillary. This effect is more significant than (a).

(d) The stress S_o required to produce flow at any point in a capillary at a distance R from the axis is given by

$$S_o = PR/2L \qquad\qquad (I)$$

where P is the applied pressure, and L is the capillary length. Near the axis R is very small so that P would have to be infinitely large for $PR/2L$ to exceed S_o. This is not possible under experimental conditions. Therefore, there is always a thin layer of sample near the axis which moves through the capillary as a solid plug ("plug flow").

Detailed discussion of corrections to be made for the above, and other, phenomena is found elsewhere (3).

When deriving the equation for flow in a coaxial cylinder viscometer, only the forces exerted by the sample on the curved surfaces of the cylinders are considered. However, if the inner cylinder is wholly immersed, forces are also exerted on both its ends. If the upper end of the inner cylinder is left uncovered the effect due to the lower end can be estimated by immersing the inner cylinder to different levels in the sample and measuring the ratio torque/angular velocity. When this ratio is plotted against the depth of immersion (i) a linear relationship should be obtained which gives a negative intercept on the i axis. This represents the correction to be added to i.

Newtonian viscosity data obtained with a falling sphere viscometer

are interpreted by Stokes's law for a sphere descending through a liquid at constant speed. If the sphere is large in comparison with the diameter of the tube through which it falls a more complex equation has to be used. Recently, Scott-Blair and Oosthuizen (4) have shown that several tests can be made on a single sample provided very small spheres are used. By rotating the tube carefully between tests unsheared material becomes available for further tests. Systems deviating only slightly from Newtonian behaviour can also be examined by using spheres of different radii and densities (5).

The ultrasonic viscometer operates on principles which are different from those of other viscometers. A probe and an electronic computer are the essential components. At the end of the probe is a thin alloy steel blade which is excited by a short electrical impulse, so producing ultrasonic shear waves in the medium around the probe. The energy involved in shearing the sample is translated into viscosity units by the computer. Whilst this instrument lends itself to automatic control of η, and detection of deviations therefrom, its application is limited to Newtonian fluids since only one rate of shear is available.

Table III summarizes the equations required for calculating v, S, η, and yield value, from data acquired with the principal types of viscometers discussed in this section. Corrections for "end effect," kinetic energy, etc., should be introduced where necessary. In capillary viscometers both S and v vary from O at the centre of the capillary· to a maximum at the wall. When considering non-Newtonian flow it is customary to base the calculation on conditions prevailing at the capillary wall.

Co-axial and cone-plate viscometers are particularly useful for studying the consistency of semi-solids since they offer a wide range of v extending down into a region of very low shear. The latter, i.e. < 1 sec^{-1}, is suitable for studying stationary structure. For many practical purposes the Haake "Rotovisko" is the most versatile instrument as it comprises both coaxial and cone-plate viscometers. The Weissenberg rheogoniometer offers facilities for both rotational and oscillatory shear. Oscillatory shear is particularly useful for studying structure since small amplitudes affect structure to a lesser extent than complete rotation.

Study of "stationary" structure

Rheological studies are not restricted to measuring η. Other parameters can be derived for a disperse system by studying the creep behaviour in a low shear coaxial cylinder viscometer. In one form of the instrument
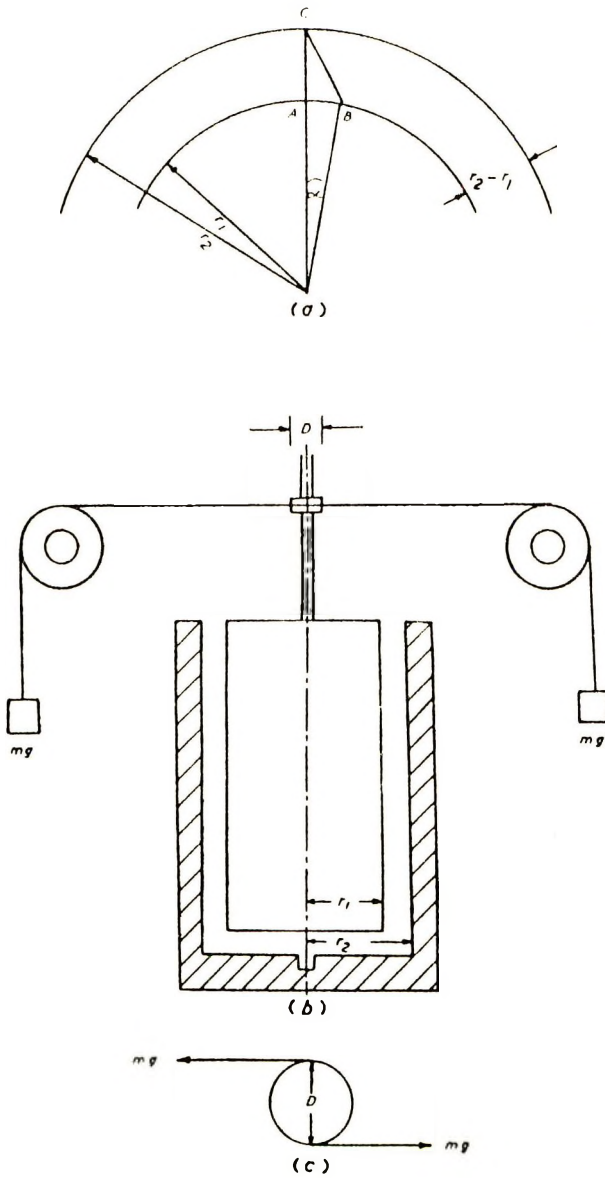
Figure 3   The Calculation of Creep Compliance

(*Fig. 3*) the surfaces of both cylinders are finely ribbed to prevent sample slippage.   The outer cylinder is kept stationary while the inner cylinder is rotated slowly by a pulley-weight arrangement.   Angular rotation of

the inner cylinder is measured optically by reflection of a light beam from a lamp via a mirror affixed to the inner cylinder suspension wire on to a graduated scale.

$$\text{Strain } (\psi) = \frac{r_1 a}{r_2 - r_1} \tag{II}$$

where r_1 and r_2 are the respective radii of the inner and outer cylinders, and a is the angular rotation.

$$\text{Shear stress (S)} = \frac{mgD}{\pi(r_1 + r_2)\,d} \tag{III}$$

where m is the weight acting over each pulley of diameter D, and g (981 dynes) is acceleration due to gravity.

$$\text{Creep compliance} = \frac{\psi}{S} = \frac{r_1\,a\pi\,(r_1 + r_2)\,d}{(r_2 - r_1)\,mg} = K\frac{a}{m} \tag{IV}$$

since a and m are the only variables.

From the way in which creep compliance changes with time, it is possible to make a detailed rheological analysis. The calculations involved are discussed in full in the section dealing with the parallel plate viscoelastometer.

PENETROMETERS

A needle or cone (or sphere) penetrates the sample with a given force for a predetermined time, and the depth of penetration is measured. The main difficulties with this technique are that the area of contact between penetrometer and sample does not remain constant during the test, and that sample is displaced in a direction opposite to that in which the penetrometer moves.

Yield value (S_o) for a cone penetrometer, e.g. Hutchinson, which is operated by a release mechanism is calculated from depth of penetration (p cm) by

$$\frac{S_o}{(\text{gm/cm}^2)} = \frac{K_1\,mg}{p^n} \tag{V}$$

where m is the weight (gms) of the cone plus mobile parts, and n is a constant with a value depending on the properties of the sample being tested, and usually approximating to 2 (8).

$$K_1 = \frac{1}{\pi} \cos^2 \alpha \cot \alpha \tag{VI}$$

where 2α is the cone angle.

The original Institute of Petroleum grease testing cone (9) comprised a small angle (30°) cone superimposed on a wide (90°) angle cone.   With this type of cone the geometry of the system becomes complicated when the penetration depth exceeds the height of the 30° cone, and equations (V) and (VI) are no longer applicable.   A smooth, single angle cone overcomes this fault (10).   For long service it can be made of aluminium with a tip of hard steel.

Investigations with cones of different angles (11) gave the following relationship

$$p \ tg \left(\frac{\alpha}{2}\right) = K_2 \tag{VII}$$

where K_2 is a constant.   Reproducibility is most satisfactory when p is restricted to 7.5 – 20 mm.

Haighton classifies materials according to S_0 by the general scheme shown in *Table IV*.

Table IV   Textural Classification of Materials according to Yield Value[10]

Yield value (gm/cm²)	Assessment
<50	Very soft to just pourable
50 – 100	Very soft, not spreadable
100 – 200	Soft, but already spreadable
200 – 800	Plastic and spreadable
800 – 1000	Hard, but satisfactory spreadable
1000 – 1500	Too hard, limit of spreadability
>1500	Too hard

The rod penetrometer consists of a metal rod surmounted by a small platform.   The base of the rod is brought into contact with the surface of the sample, and the depth, or rate, of penetration determined for different loadings of the platform.   If the load is converted into shearing stress, and penetration into velocity gradient, then, in the case of non-Newtonian flow, a curve will be obtained corresponding to that for pseudoplastic or plastic flow as shown in *Fig. 2*.   A similar type of curve is obtained with the cone penetrometer using cones of different weights.

Pseudoplastic flow can often be defined by

$$v = \frac{1}{\eta^*} \cdot S^n \tag{VIII}$$

where n is a constant.

If a yield value is observed equation (VIII) becomes (12)

$$v = \frac{1}{\eta^*} (S - S_o)^n \qquad \text{(IX)}$$

Equation (IX) reduces to Bingham's equation for plastic flow when n = 1. In all other cases η^* is not the same as the true viscosity η, nor does it have the dimensions of viscosity. When $n \neq 1$, the sample is said to exhibit "quasiflow." Many criticisms have been levelled against equations (VIII) and (IX) since they can be made to fit most curves by suitably adjusting the values of the constants. Furthermore, when S changes, n sometimes alters; η^* may also be affected.

COHESION

Interest in the stickiness, or tackiness, of materials led to the design of an instrument to measure the force required to pull a movable plate away from a stationary plate when a thin layer of sample is sandwiched between them (13,14). This principle has proved useful for measuring the increase in tackiness which occurs when lotions and ointments dry after rubbing into the skin (15).

Two kinds of forces are involved in these measurements, viz. cohesion between the individual particles, and adhesion between the sample and plates. When cohesion exceeds adhesion, rupture occurs at the surface of the sample in contact with the movable plate, thus providing a measure of stickiness. Alternatively, if adhesion exceeds cohesion, rupture occurs within the sample itself, and one derives a measure of the internal strength.

Some materials show decreasing stickiness with increasing stiffness. Their consistency can be examined with an instrument (16) of the basic design shown in *Fig. 4*. The sample is deposited in a Petri dish and the surface is carefully levelled and smoothed out. A circular steel plate of smaller diameter than the dish, which is connected by a vertical rod to two cords via metal rod junctions and an Oldak gauge, is brought carefully into contact with the upper surface of the sample. The upper cord is attached to an axle which applies an upward force to the steel plate when rotated by a constant speed motor. This force causes a metal plate, which passes through the lower metal rod junction, to bend in the centre since it is fixed towards its extremities over two knife edges. The deformation is recorded by the gauge. The maximum reading recorded, viz. when the upward acting force just exceeds the cohesion, is related to the strength of the material.
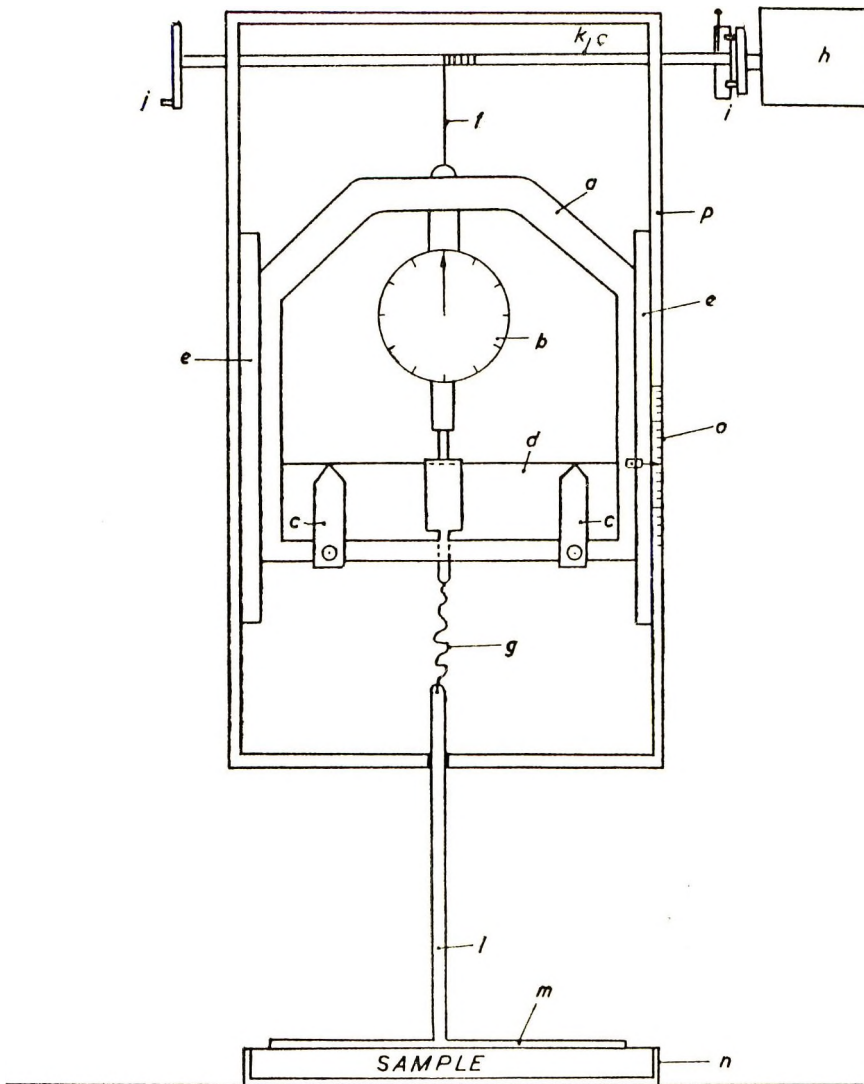
Figure 4 Stickiness meter.

(a) Movable framework. (b) Gauge for measuring deflection of spring (d). (c) Adjustable knife edges. (d) Spring. (e) Grooves. (f) Upper cord connecting axle (k) to framework. (g) Lower cord connecting framework to test body (m). (h) Motor. (i) Gear. (j) Handle. (k) Axle. (l) Rod. (m) Test body. (n) Container for sample. (o) Scale. (p) Fixed frame.

The sample draws out into a "neck" as the axle rotates and pulls up the cord. This neck progressively thins in the middle and eventually ruptures, leaving a layer of sample on the underside of the metal plate.

Only "single point" determinations can be made with the apparatus in this form.   To study non-Newtonian flow behaviour the constant speed motor is replaced by a balance pan on which different weights can be placed.   The time (t) taken for rupture over a wide range of pan loadings (mg) is determined.   A plot of mg against 1/t gives a curve characteristic of non-Newtonian flow (*Fig. 2*).

Under these conditions the viscosity equations for the linear portions of pseudoplastic (η_p), and plastic flow (η_{pl}), curves are

$$\eta_p = \frac{(T + c)^2 \text{ mg } 4.6 \text{ t}}{\pi R^4} \tag{X}$$

and

$$\eta_{pl} = \frac{(T + c)_2 \text{ (mg} - \text{i) } 4.6 \text{ t}}{\pi R^4} \tag{XI}$$

where T is the sample thickness, c is a constant with a value which is determined by trial and error, R is the radius of the metal plate, and i is the intercept on the mg axis in the mg – 1/t plot.

The consistency of semi-solid materials may be examined also by shearing a thin layer between two parallel vertical plates (17), one of which is stationary while movement of the other is activated by a loading device.

PARALLEL PLATE VISCOELASTOMETER (18)

A rectangular block is cut with the sampling device shown in *Fig. 5a*. It is fitted with a plunger for easy removal of the sample, which is then cut into two equal halves.   The pieces S_1 and S_2 are placed on either side of a thin ribbed metal plate D (*Fig. 5b*) and then introduced between two ribbed plates A and B.   Plate A is stationary, but B can be brought into contact with the upper surface of S_2 by carefully tightening with the screw device.   One end of D is connected to a balance pan W by a cord which passes over two low-friction pulleys P and P_1.   When W is loaded S_1 and S_2 are subjected to shear, the magnitude depending on the weight used. The surfaces of S_1 and S_2 in contact with A and B remain stationary, while the maximum shear is experienced by the surfaces in contact with the two sides of D.   Shear in this latter region depends on the rate at which D moves; this is followed by a travelling microscope focussed on the knife edge K.   To ensure minimal breakdown of sample structure, the maximum movement of D should not exceed a few mm.   If temperature control is desired the apparatus can be mounted in a box made of polystyrene foam $1\frac{1}{2}$–2″ thick, which contains a heating or cooling unit.
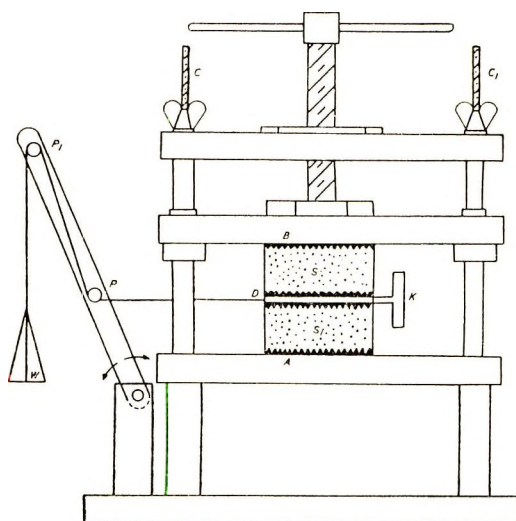
Figure 5a Creep Apparatus

A,B,D, Ribbed plates. C.C₁. Constant compression devise. S.S₁. Samples.
P.P₁. Pulleys (Low friction). W. Weight pan. K. Knife edge.
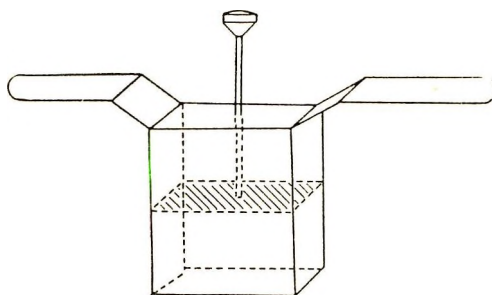
Figure 5b Sample Cutting Device.

Solid materials which are essentially disperse systems give a creep compliance – time curve indicative of viscoelastic behaviour (*Fig. 6*), i.e. they behave like solids in the initial stages of shear, and subsequently they exhibit fluid behaviour "in the sense that work of shearing deformation is not completely conserved, as in solids, nor is it completely dissipated as in fluids" (19).
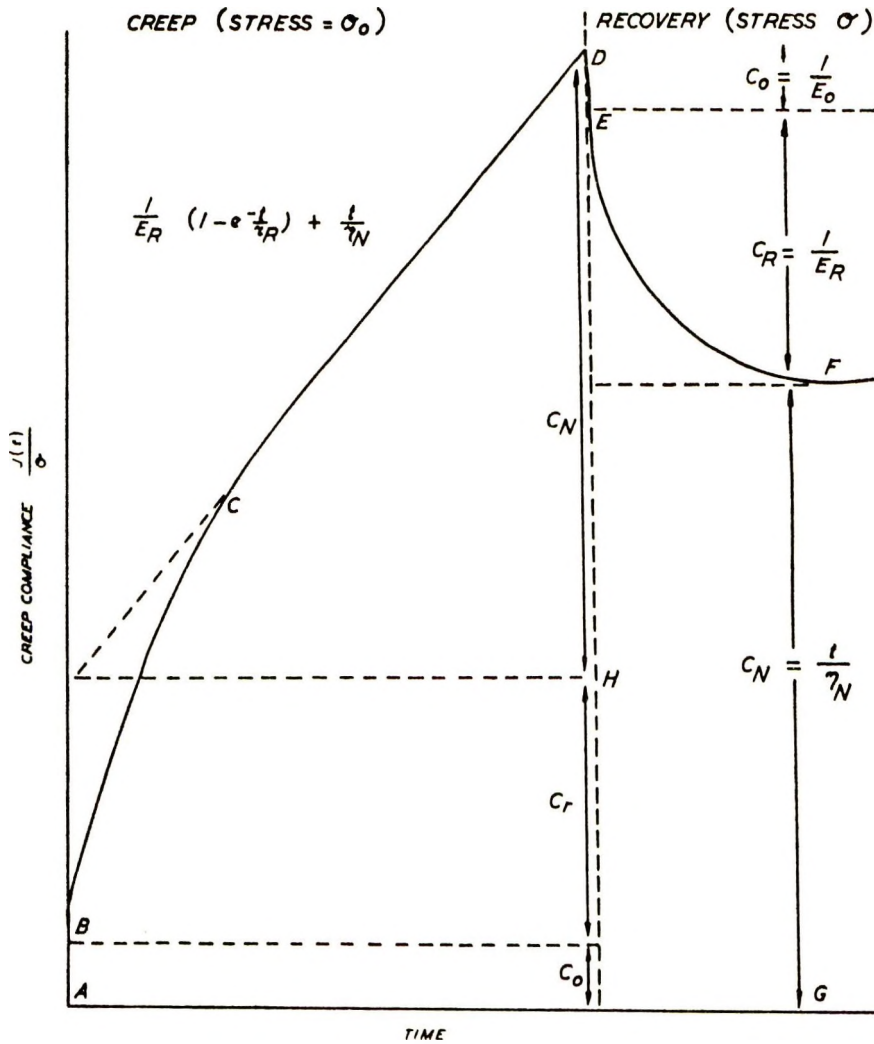
Figure 6 Model creep curve.

The creep curve has an overall creep compliance $J(t)/\sigma$ at any time t, where J is shear strain, and σ is shearing stress.

$$J = \frac{\beta f}{h} \tag{XII}$$

where β is the displacement observed with a travelling microscope having a reciprocal magnification factor f, and h is the thickness of S_1 and S_2.

$$\sigma = \frac{F}{2A} \tag{XIII}$$

where F ($= mg$) is the load placed in pan W, and A is the cross-sectional area of S_1 and S_2.

The creep compliance curve (*Fig. 6*) can be sub-divided into three distinct regions.

(1) A region of instantaneous elastic compliance (A – B) with a modulus E_o, in which bonds are stretched elastically. If shear does not continue beyond this point, recovery is complete when stress is removed. The instantaneous elastic compliance is given by

$$C_o = \frac{1}{E_o} = \frac{J_a(t)}{\sigma} \tag{XIV}$$

where J_a is the instantaneous elastic deformation.

(b) A region of retarded elastic compliance (B – C) with an elastic modulus E_R, viscosity σ_R, and retarda tiontime τ_R ($= \eta_R/E_R$), in which bonds break and reform. Actually, bonds do not all break and reform at the same rate so that all three parameters should be replaced by spectra showing a wider distribution of values. Present discussion will be restricted to the simplest model.

$$C_R = \frac{1}{E_R} = C(1 - e^{-t/\tau_R}) = \frac{J_b(t)}{\sigma} \tag{XV}$$

where J_b is the retarded elastic deformation, and C_R represents an average of all the compliances involved.

(c) A region of Newtonian flow (C – D) with viscosity η_N. Once the bonds have ruptured, i.e the time for them to reform is longer than the test period, individual particles or units flow past one another.

Newtonian flow is proportional to the time of loading, so that

$$C_N = \frac{t}{\eta_N} = \frac{J_c(t)}{\sigma} \tag{XVI}$$

where J_c is deformation in the Newtonian region. Thus, the slope of the linear part of the curve is equal to $1/\eta_N$.

The overall compliance for the whole creep curve is, therefore,

$$\frac{J(t)}{\sigma} = C_o + C_R + C_N = C_o + C(1 - e^{-t/\tau_R}) + \frac{t}{\eta_N} \tag{XVII}$$

Where $t \to O$

$$\frac{J(t)}{\sigma} = C_o \tag{XVIII}$$

Since C_o and η_N are now known C_R can be calculated from equation (XVII).

Equation (XVII) can be written in the form

$$\frac{-t}{\tau_R} = \frac{-t}{C_R \eta_R} = \ln \left[\frac{J(t)}{\sigma} - C_o - C - \frac{t}{\eta_N} \right] \qquad (XIX)$$

If the right-hand side of equation (XIX) is plotted against t, the slope of the line represents $- 1/C_R \eta_R$, so that η_R and τ_R can be calculated since C_R is known.

In this way all parameters associated with the near-stationary structure of a solid material, and the effect of recipe modifications, processing, etc., can be studied. This technique has proved suitable for investigating soap texture.

MODULUS OF RIGIDITY

The main advantage of this test (20) for materials showing a high degree of elasticity is simplicity of the apparatus required. It consists of a glass capillary U-tube, one arm of which opens up into a wider bore tube, while the other capillary arm is graduated in mm (*Fig. 7a*). The tube is filled with mercury to the base of the wide-bore tube, and a fixed volume of sample is then introduced into the latter. In the case of a gel 20 ml of the warm solution is pipetted through the opening of the wide bore arm, and allowed to set overnight under careful temperature control.

The sample is subjected to variable shear conditions by using air pressure, and the resultant displacements cause the mercury to move up the graduated capillary arm. Air pressures are registered with a mercury manometer.

Provided L is very much larger than R

$$G = \frac{PR^4}{8LB^2H} \qquad (XX)$$

$$\text{maximum strain at the tube wall} \quad = \quad \frac{4Q}{\pi R^3} \qquad (XXI)$$

$$\text{maximum stress} \quad = \quad \frac{PR}{2L} \qquad (XXII)$$

where G is modulus of rigidity, P is the net applied pressure, i.e. corrected for the back pressure of mercury, L and R are the length and radius respectively of the cylindrical column of sample, B is radius of the capillary tube along which the mercury moves, H is displacement of the mercury meniscus, and Q is the volume displaced.

The above apparatus is suitable for measuring high values of G.
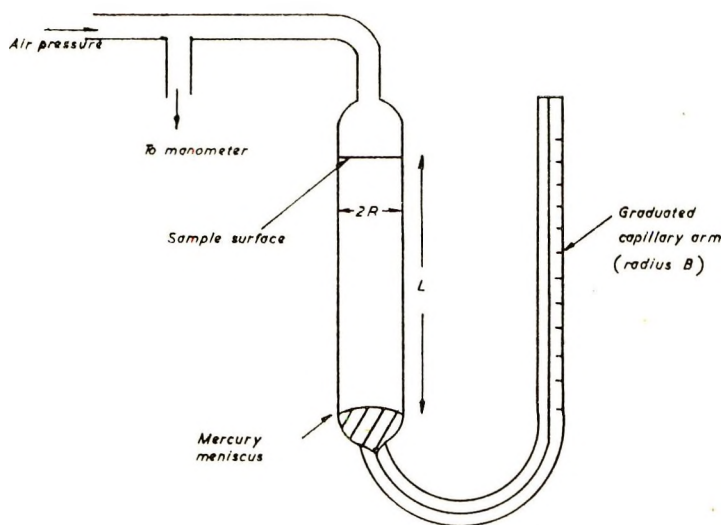
a) *Saunders and Ward's method for determining rigidity of hard gels.*
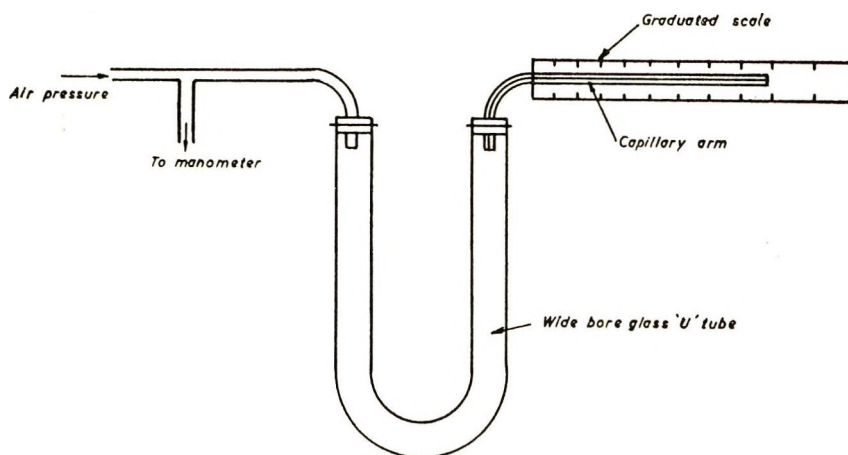
b) *Modified technique for determining the rigidity of soft gels.*

Figure 7

G should be measured over a wide range of strains since it may be influenced by strain in the same way as gelatin gels.

For softer gels with much lower values of G, and where the deformations under stress may not be all elastic, a modified technique can be used (21). In this case the whole U-tube consists of wide bore glass ($\sim$1.5 cm diameter), and the arm to which pressure is not applied is attached to a nearly horizontal capillary (*Fig. 7b*) containing a drop of coloured alcohol. Movement of the alcohol along the capillary is proportional to displacement of gel in the U-tube under different air pressures. This procedure has proved suitable for rheological measurements on a hair dressing with "a distinct bounce due to its high degree of viscoelasticity," and other cosmetic products (15).

When using either apparatus one must ensure that movement of indicator fluid results only from sample deformation, and not from sample slippage along the walls of the tube.

The tensile strength of gels, and materials of similar consistency, can be estimated by extruding from a variable pressure viscometer fitted with a nozzle of 2–14 mm, and determining the quantity falling off under its own weight (22). Tensile strength is given by the ratio sample weight extruded/nozzle area. For thixotropic gels tensile strength is related to the time dependence of viscosity.

Recently (23) a correlation has been observed between palate assessment of gum solutions and their rheological properties. Gums which feel very slimy in the mouth are usually only slightly non-Newtonian. As non-Newtonian behaviour becomes more developed the degree of sliminess decreases.

SECTILOMETER

The consistency of solid materials can be determined with this instrument (24).

A fine wire held taut in a metal frame constitutes the cutting device (*Fig. 8*). A sample of standard dimensions is placed on a support platform, and its surface is brought into contact with the wire. By mechanically moving the platform upward at a very slow, steady, rate (e.g. 0.07 cm/sec), the wire cuts through the sample. The thrust on the wire is transmitted by the metal frame to a lever balance, where it is registered.

This technique is not suitable for very soft materials because the wire does not cut through the sample until a minimal thrust has been developed. For a sample width of 3 cm this may be as much as 40 g.
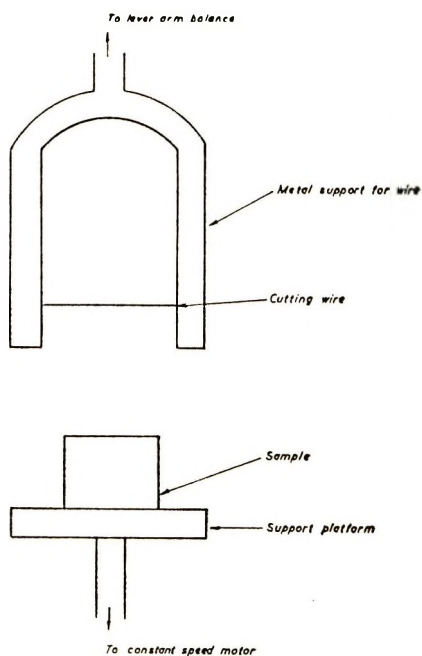
Figure 8 Sectilometer for assessing the consistency of solid materials.

In another version of this sectilometer (11) the sample is placed on the pan of a spring balance, and the wire, motivated by a constant speed motor, cuts through it at a rate of 0.044 cm/sec. The force exerted on the sample is recorded by the spring balance.

COMPRESSION BETWEEN PARALLEL PLATES

In this test, solid materials are subjected to alternate compression and relaxation between parallel plates. The technique is less sensitive than that described under Section 4, and involves more structural breakdown.

The sample is placed on a solid metal core with a flat surface which is fastened to the base of a metal stand, and a metal plate is brought gently into contact with its surface (*Fig. 9*). If the sample is of cylindrical shape, the plate should be circular; if the sample is a rectangular block, the plate should also be rectangular. The plate is connected by a metal rod to a platform on which weights can be placed. Loading is by means of slotted weights placed around a holder plate which is gently lowered, by a pulley device, on to the platform. In this way damage to the sample is minimized at the moment of loading. A travelling microscope, focussed
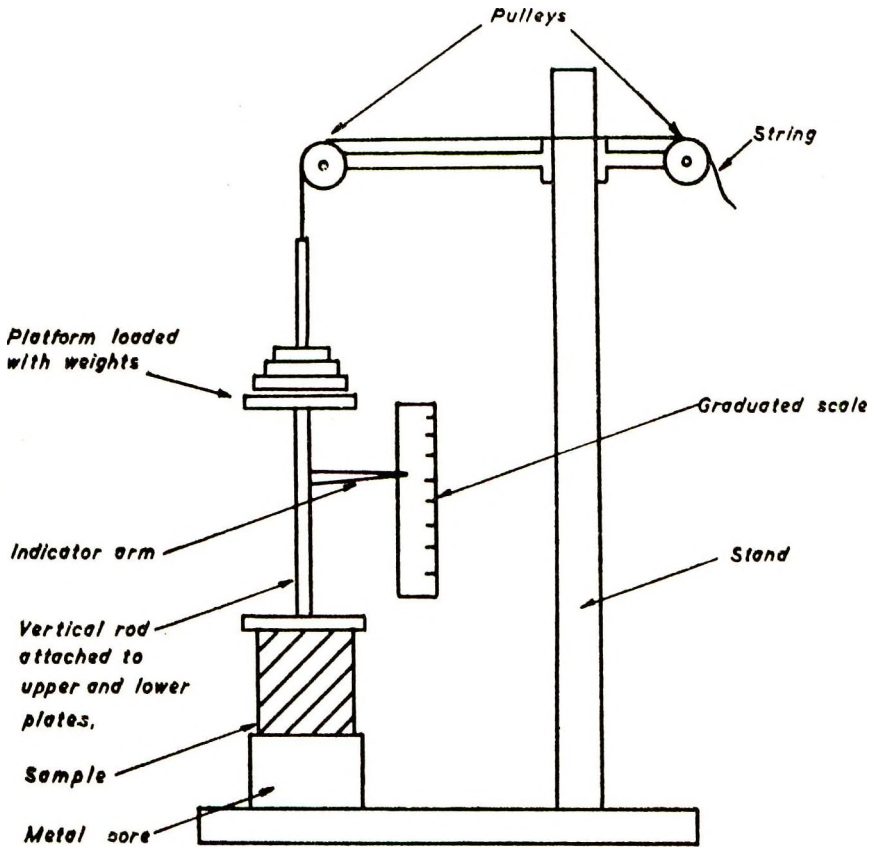
Figure 9　Compression between parallel plates.

on an indicator arm attached to the vertical rod supporting the platform, measures the rate of compression during loading and subsequent recovery when the load is removed.

The applied load (F) is converted into stress per unit area (U) by

$$U = \frac{F}{A} \cdot \frac{H_o}{H} \qquad \text{(XXIII)}$$

where H_o and H are the height of the sample before and after deformation respectively.

$$\text{Shear stress } (\sigma) = \frac{U}{3} \qquad \text{(XXIV)}$$

$$\text{Strain (T)} = \frac{e}{H_o} \qquad \text{(XXV)}$$

where e is the non-recovered part of the deformation.

The data can now be treated in the same way as creep compliance data (Section 4) by plotting T/σ against t, but the calculation of viscosity has to be modified since compression produces viscous flow in more than one direction.   An approximate correction can be achieved by multiplying the calculated viscosity by $2\pi(H_o)^2/A$.   Calculated parameters are lower than those derived from creep compliance since the compression technique causes more structural alteration to the sample.   The weight required to give a reasonable compression should be determined by trial and error prior to carrying out the main tests.

In a cruder form of the present test, the rate of compression is not determined, but only the total compression, and overall recovery, after a suitable time e.g. 3–5 min.

OTHER RHEOLOGICAL TECHNIQUES

The other, more sophisticated, procedures listed in *Table I* for assessing the consistency of solids require more complex equipment and are more time-consuming.   They are suited only to basic research.   Ferry (25) reviews these methods in some detail.

CONCLUSIONS

It is often possible to use more than one technique to measure the consistency of any material.   However, the techniques employed may not all measure the same component of texture, and this should be appreciated when attempting to correlate the various groups of data.   For example, ease of spreadability arises from rapid deformation and structural breakdown.   Firmness depends on the ability to resist static, or virtually static, loads, so that it is related to very slow deformation.   Thus, firmness and spreadability represent quite different attributes of the textural quality described broadly as consistency.   Penetrometers, and shear or compression under small loads, measure firmness.   Extrusion, and other methods involving appreciable structural breakdown, measure spreadability.

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DISCUSSION

MR. A. MOËS: When one establishes with the aid of a viscometer the rheogram of a non–Newtonian fluid, for example pseudoplastic, can one tell from a graphical interpretation, or by calculation, the viscosity of this fluid at rest, i.e. for a rate of shear equal to zero, or for very low stresses such as those induced by solid particles settling in the vehicle?

THE LECTURER: No, because it could well be that the pseudoplastic at rest is in fact not showing any viscosity, it might only have elasticity. A pseudoplastic at rest system consists of particles, or individual components, which are linked together, and as the rate of shear is increased this attraction is progressively broken down until eventually each of the particles acts independently, and simple Newtonian flow prevails. The structure at zero rate of shear is, however, quite different. Therefore by measuring the condition where there is complete breakdown and independent flow of particles, one obviously cannot get any information of the stationary structure where one has interaction and linkages between the particles.

MR. MOËS: Could you tell me if a particular method exists to investigate the structure of sediments of flocculated particles in coarse suspensions?

THE LECTURER: One of the methods is described under the heading of "Study of Stationary Structure" (page 446). This gives a simple method, involving a quite easily designed coaxial cylinder viscometer, for studying the elasticity of the structure in the steady state where there is linking between the particles. If one does not want to become so academic there is another method which can be carried out with a suitable commercial viscometer, where one first of all subjects the system to very high rate of shear to break down all the structure and get Newtonian flow, and one can then measure the rate of recovery of the structure at a very much lower rate

of shear.   One normally finds, for this very low rate of shear, if plotting the viscosity of the system against time, that initially the viscosity will be a minimum but it then will gradually build up with time to a steady maximum value.   In the case of a simple w/o emulsion of medium concentration this takes something like 30 sec, but nevertheless one can get quite a number of readings in between.   With pigment and other materials present in the continuous phase it takes rather longer.   One then applies an equation to this data to find out what apparent volume fraction of material is actually present, i.e. one has the original particles which will once again link up in the stationary state.   I am assuming that all the particles are approx. the same size but this need not be the case–and in between the particles one gets a certain amount of liquid which is bound to be held within the particles; therefore the effective volume fraction disperse phase is higher than the actual volume of particles present.   This apparent volume fraction can be determined from the equilibrium viscosity at the low rate of shear.

This method was originally introduced by Mooney (26), who gave an empirical equation for determining the theoretical relationship between viscosity and volume fraction.   All he did was to take this equilibrium viscosity measurement, transfer it to this graph, and find the apparent corresponding volume fraction.   This was always higher than the theoretical value, and it gives some idea of the amount of liquid held within the aggregates. But unfortunately Mooney's equation was a very empirical one, he did not appreciate that particle size has a great influence.   Because his equation held for some old data, he assumed that it could be applied to systems with quite different particle sizes, which is not true.   I have discussed this question (7) and given an alternative equation which can be used.

Mr. N. J. Van Abbé: It seems to me that rotational viscometers, which are quite elaborate and expensive instruments, are basically dependent upon delicate mechanisms such as torsion springs.   How often should calibration checks be made?

The Lecturer: Most of the instruments described are quite simple, possibly apart from the commercial viscometer.   The one described in p. 447 operates on a coaxial cylinder principle with a simple torsion wire.   Obviously with any instrument one must periodically check whether the wire or spring is functioning correctly. It can be replaced and one can still get reproducible results.

This raises just one point.   Very often it is extremely difficult to reproduce a particular consistency.   Even within a single batch of material there might be a wide range of consistencies, e.g. in a simple, spherical, baked cake, consistency measurements at different points reveal a wide variation from the centre to the outside of the cake.   This complicates matters because one is never certain that a stating panel and the instrument are testing the same product.

Mr. R. Clark: Certain toilet preparations are now being consumed in sufficient quantities to merit their consideration for production by continuous methods, toothpaste for instance.   Which of the various techniques mentioned would you recommend as a continuous viscometer for simple process control?

The Lecturer: This is a very old problem for which there is no solution at present.   The only instrument I know of which will function satisfactorily in a pipeline is the *Ultraviscoson* viscometer, but unfortunately this is only suitable for

(26) Mooney, M. *J. Colloid Sci.* **1** 195 (1946).

measuring Newtonian viscosity.   As far as I know there is nothing available for non-Newtonian measurement.

DR. A. W. MIDDLETON: In page 458 you refer to a correlation between palate assessment of gum solutions and their rheological properties.   Can you explain how this correlation was derived?

THE LECTURER: As far as I can remember people were asked to estimate the degree of sliminess of the gum solutions presented to them, and rheological studies were simultaneously carried out on these solutions.   They did find by statistical correlation that there seemed to be a relationship between the degree of sliminess and the degree of non-Newtonian behaviour of the material.   The number of materials examined at the time, however, was quite limited, so I do not know whether this reported opinion would have very wide application.

DR. A. W. MIDDLETON: Would the errors be likely to occur in the assessment of the subjective relations?

THE LECTURER: Yes.   From the little experience I had with gum solutions and similar things, they are very difficult to reproduce in consistency, unless one very carefully follows a standardized procedure and allows the solutions to age for a certain given time before testing.   This certainly applies with gelatine.

DR. A. R. ROGERS: What methods do you use for studying distribution of sizes in the 1μ and less range?

THE LECTURER: At the moment we are able to see those which are just below 0.5μ under the microscope, but we have no accurate method of determination; I understand that Dr. Otterwill developed a method based upon light scattering principles which enable him to do this for polystyrene latex particles.   These, of course, are different, but we are hoping to examine something along these lines next year.   One of the major difficulties, even when you are able to measure these sizes, is how to find the average size.   In all methods of calculating average size, apart from doing a pure arithmetical mean, one gets involved in summing the powers of the particle size, and all these submicroscopic sized particles would just cancel out.   I have been thinking about this subject of late, because it is very important to our rheological studies.   Possibly in order to show the effect of these submicroscopic sized particles one should calculate not a mean, but a reciprocal mean diameter, and then the very small particles would play a much larger part than the larger ones, which is the right order.

DR. J. J. MAUSNER: What would be the best method for measuring the spreadability of thixotropic gels?

THE LECTURER: Any method which will enable you to measure viscosity at very high rates of shear.

DR. J. J. MAUSNER: Is that a matter of spreadability?

THE LECTURER: I imagine that one would get a drastic breakdown of any structure which is present in the material, and this would be the same as the conditions prevailing at high rate of shear.   The problem with all the rheological methods of measurement is that one does not know what shearing conditions one is using in the practical process.   As yet no one has been able to calculate these.   One or two

years ago someone tried to calculate the shearing forces involved in certain elementary operations, such as pouring a liquid or a non-Newtonian fluid out of a bottle or extruding it from a syringe, just to get some idea of the shearing conditions which should be applied in viscosity measurements, but to date no one has gone any further than this.

Thin-layer chromatographic techniques in residue analysis

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Synopsis—Thin-layer chromatography has rapidly developed into a precise technique of considerable use to the residue analyst. This paper attempts to deal succinctly with all aspects of thin-layer chromatography, from the choice of the adsorbent to the final documentation of the developed plate. Recent advances in thin-layer chromatography, wedge-layer, multi-band layer and gradient-layer chromatography are also covered by the paper.

INTRODUCTION

The introduction of paper chromatography by Consden, Gordon and Martin (1) as an extension of the partition chromatographic technique of Martin and Synge (2) was followed by a very rapid expansion of the use of these procedures. The advantages of paper chromatography in particular, e.g. small sample size, excellent resolution and short times involved, over earlier separatory methods were so great that the accompanying disadvantages tended to be overlooked. While being admirably suitable for amino-acids and hydrophilic compounds in general, many difficulties arose when lipophilic compounds were studied. These were only partially overcome by reversed-phase paper chromatography and although the classical adsorption chromatography worked very well for materials of this nature, no general analytical technique was available.

The use by Izmailov and Shraiber (3) of a thin (2 mm) layer of powdered adsorbent, such as calcium oxide, magnesium oxide or alumina, to obtain

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chromatographic zones from a single drop of a solution of a drug by drop-wise application of a mobile solvent, passed almost unnoticed. Thin-layer chromatography as it is recognized today can be said to have begun with the work of Meinhard and Hall (4) who used starch as a binding agent in order to endow the adsorbent layers with some mechanical stability. Application of this method to the preparation of "chromato-strips" (0.5 × 5.25″) by Kirchner, Miller and Keller (5) demonstrated the usefulness of thin-layer chromatography for the separation of terpenoid compounds. They employed either starch or gypsum as binding agent and found the strips were easier to prepare and handle than the silica-impregnated filter paper they had previously used (6). Kirchner and Miller (7) also intro-duced the use of "chromatoplates" of larger size and these were used by Reitsama (8) in a study of essential oils. The thin-layer chromatography of pesticide residues also commenced at this time with the determination by Kirchner *et al* (9) of biphenyl in citrus fruits following a clean-up separation on starch-bound silica gel chromatostrips.

With the publication of the series of papers by Stahl (10-14) the uses of thin-layer chromatography became more widely recognized and readily applied. The commercial availability of the materials and apparatus he described (14) for the production of gypsum-bound layers of silica gel, alumina and kieselguhr was a big factor in promoting this growth. Today thin-layer chromatography is regarded as a necessary adjunct to all fields of analytical chemistry, not solely for its diagnostic properties but also in the preparation of pure specimens, for clean-up purposes before the appli-cation of other analytical methods of determination, in the study of rates of reaction, etc. The number of publications describing various aspects of thin-layer chromatography has risen exponentially over the past few years while five books on the subject appeared within two years.

PROCEDURES

Preparation of chromatoplates

Layering apparatus and techniques

Thin-layer chromatography depends for its success on the ability to prepare reproducibly uniform layers of the desired thickness of a suitable adsorbent upon the chosen supporting plate. While glass carrier plates are by far the most popular for this purpose, aluminium (15), stainless steel (16), and plastic materials (17), have also been used for special pur-poses. The dimensions of the carrier plates are in general governed by

the type of spreading apparatus to be used; 20 × 20 cm and 10 × 20 cm are popular sizes for use with commercial applicators but any convenient size may be suitable for hand layering.

The apparatus commercially available may be readily divided into two classes:—(a) Moving spreader, stationary plate; (b) stationary spreader, moving plate. All methods depend upon placing on the carrier plate a slurry of the adsorbent in water, alcohol or some other volatile liquid and smoothing it out to form a layer of the required thickness by some suitable means. The "moving spreader" type of apparatus is of wide versatility and is easily used by unskilled hands to prepare satisfactory chromatoplates. The apparatus of this type designed by Stahl (14) and manufactured by Desaga G.m.b.H., Heidelberg [available from Camlab (Glass) Ltd., Cambridge] is universally used for the preparation of layers up to 2 mm thick and some 2000 cm² in area can be layered in one operation. A very detailed account of its use for the preparation of chromatoplates for pesticide residue analysis has been given by Kovacs (18). One slight disadvantage of this apparatus is that the thickness of the carrier plates to be sequentially layered must be very uniform if smooth operation is to be achieved. Variations in surface level as the spreader is drawn across the plates causes "jumping" to occur with consequent irregularity of the layer thickness. An apparatus based on a similar principle is available from Shandon Scientific Co. Ltd., London, which endeavours to overcome this drawback. The template on which the carrier plates are laid consists of an inflated plastic bag which presses them against two rails, thus ensuring that the uppermost surfaces are level (19). Badings (20) has described an applicator which may be employed with plates of differing widths.

Dilute slurries of adsorbent have been sprayed on to the carrier plates (8,21), layer thickness being decided by the number of "passes" made by the spray gun across the plate. These systems have the advantage of readily allowing the use of plates of various sizes and thicknesses indiscriminately. Smooth layers are obtained in this way but the point to point variation in thickness is liable to be greater than that given by a correctly prepared plate made by using a moving spreader.

Adsorbents and binding agents

Any adsorbent which is used for columnar separations can be adapted for use as a thin-layer (or "open-column"). Kirchner *et al* (5) investigated layers of silica gel, alumina, magnesium oxide, calcium hydroxide, dicalcium phosphate, bentonite, calcium and magnesium carbonates, *Florisil, Filtrol,*

talc and starch, usually with the aid of 5% starch or 20% plaster of Paris added as a binder. Of the many possible materials, silica gel and alumina have since proved to be of widest applicability, with appreciable usage of kieselguhr and cellulose also.

Other adsorbents of more recent introduction include dextrangel, DEAE-Sephadex and acetylated cellulose (22), microcrystalline cellulose (23), ion exchange materials (24), polyamides (25) and basic zinc carbonate (20). The choice of stationary phases for thin-layer chromatography has been discussed by Schorn (26), and reviewed by Mangold (27) and Russell (28).

Reactivation of the layer

Following the spreading of the adsorbent slurry over the carrier plates, these are usually left in a horizontal position at ambient temperature until the surface takes on a matt appearance (10–20 min). The manner and degree of reactivation then required will depend upon the adsorbent and the purpose for which the chromatoplates are required. The one important fact is that a definite procedure must be chosen and adhered to if consistent results are to be obtained. It has been shown (29) that during the heating of silica gel at 110°C the activity at first falls, being at a minimum after about 15 min, and then rises to a maximum value at about 30 min, remaining constant thereafter. Alumina requires higher temperatures in order to reach its maximum adsorptive power, Bäumler and Rippstein (30) heated for 4 hr at 200–220°C to obtain an activity equivalent to Brockman II. At these temperatures, however, the binding power of gypsum tends to fail, dehydration to the hemihydrate beginning at about 120°C while formation of the anhydrous salt occurs over the range 150°–200°C. For these reasons it is preferable to activate at 120°C when using alumina G although consistency of activation is not as good as that given by silica gel at this temperature.

Special applications

Preparative-layer chromatography

The use of chromatographic techniques for the preparation of pure specimens of organic compounds has until comparatively recently been confined to columnar separations. The introduction of gas-liquid chromatography on a preparative scale has been invaluable in many cases but its use is limited to compounds that are stable at the temperatures required to ensure their volatility. Thin-layer chromatoplates offer an excellent

means of preparing pure specimens of substances available in limited quantity. Where larger samples are required the usual 250 μ thick layer is inadequate as its acceptable load is limited. Increasing this thickness to 1 mm or more assists considerably (31), but many 20 × 20 cm chromatoplates must be developed to obtain reasonable quantities, acceptable loads being 5 to 25 mg/1 mm thickness of adsorbent. Equipment has now been described (32) which employs carrier plates 1 m long by 20 cm wide on which layers up to 4 mm thick can be spread, either by a moving spreader of increased capacity or by "casting" the layer *in situ* within a framework. Apparatus using carrier plates 40 × 20 cm has been advocated by Stahl (33). In practice 2 mm thick layers have been found to possess optimum properties in respect of ease of preparation, adhesion of the layer and uniformity of resolution. Samples are applied as a streak along one edge of the chromatoplate and up to 5 such plates may be developed at one time in a stainless-steel tank; multiple runs are frequently necessary to obtain suitable resolution. Fluorescent indicators are used as visualization agents since they do not affect the separated compounds. The observed bands are marked under UV illumination, scraped from the carrier plate and extracted with a suitable solvent to recover the purified specimen. In this way very pure materials can be obtained, up to 1 g per chromatoplate being a practical amount provided that good resolution from associated impurities is obtained.

When using thin-layer chromatoplates for pesticide preparative purposes on a micro-scale, with a view to subsequent electron-capture gas-chromatographic examination, it is preferable to pre-extract the adsorbent with ether to remove interfering impurities before spreading the layer. Several solvents may be used to elute the pesticide from the layer adsorbent after developing the chromatogram. In general, hexane is the solvent of choice for organo-chlorine pesticides, while for the elution of organophosphorus pesticides dichloromethane has been found preferable, recoveries ranging from 70 to 100% at levels from 10 to 80 μg (34).

Wedge-layer chromatography

The advantages of the greater acceptable load of thick preparative chromatoplates and the high R_F values and greater resolution of thin (100 μ) layers have been combined in the properties of wedge-layer chromatoplates which were designed for residue clean-up purposes (35). In this development the cross-section of the spread layer is not uniform but it is wedge-shaped, tapering from 2 mm to less than 100 μ. Such layers are spread

by simple adaption of commercial layering apparatus. For the Desaga spreader a *Perspex* trapezium, 210 mm long with vertical sides of 40 and 38 mm, replaces the normal calibrated applicator plate. Other models of spreader are more simply adapted by adjusting the smoothing edge to feeler gauges of different thickness at either end, a sloping edge being thus ensured.

In use the sample extract is applied as a streak parallel to the edge of the chromatoplate at which the layer is thickest and about 2 cm from it. After a further period of activation to ensure maximum clean-up the chromatogram is developed by the ascending-solvent techniques in the usual way. The use of this technique in the determination of traces of dinoseb has been described (36); the procedure has also been shown to be suitable for organo-chlorine and organo-phosphorus pesticides whose R_F values on silica gel are normally at least 0.50 when developed with a fairly non-polar solvent. This system is particularly of value where the ratio of co-extractives to pesticide residues is high.

Wedge-layer chromatoplates composed of silica gel G, alumina G and kieselguhr G and mixtures of any two of these materials have been prepared and examined for pesticide residue analysis. Mixtures of silica gel with either alumina or kieselguhr were prone to cracking across the wedge, though this was without any marked effect upon their chromatographic properties. Alumina and kieselguhr appeared to be of closer physical properties and mixtures of these materials did not show this cracking; they also showed useful adsorptive characteristics.

Multi-band chromatography

The use of multi-band or panel-layered chromatoplates has proved very useful both for diagnostic and for clean-up purposes (37). By inserting close-fitting partitions of suitable materials, e.g. PTFE, cork, aluminium, etc., into the body of the spreading apparatus it is possible to prepare chromatoplates composed of 2, 3 or 4 parallel panels of different adsorbents. Suitable positioning of the partitions enable panels of various widths to be layered on appropriate areas of the carrier plate. The fluid mixes of adsorbent are prepared in the usual way and are poured simultaneously into the required compartment, the assistance of a second operator being required if more than two panels are to be layered.

Panel-layered plates can obviously be developed in two distinct ways. By spotting the sample and a known standard onto each of the panels and developing vertically up the bands, a useful diagnostic system is

apparent. In this way it is possible to compare R_F values on several adsorbents developed in one mobile solvent under identical conditions of time, temperature, solvent-vapour equilibrium, etc. Including a known dyestuff, with both sample and standard, as a reference material makes it possible to correct R_F values for any hold-up due to co-extractives. Under these conditions relationships between the corrected R_F values on, say, three different adsorbents may be taken as indicative of the identity of the unknown compound, this being more positive than using one adsorbent only.

The second manner of use, i.e. development across the panels, adds to the usefulness of these chromatoplates. Sequential elution from a highly adsorptive layer onto a less active panel enhances the general resolution of compounds and is valuable for clean-up purposes. An opposite effect is observed when developing from an adsorbent of low activity to a more adsorptive material. This similarly has uses in limiting the likely position of unknown compounds on the chromatoplate, a tight band being formed at the junction of the two adsorbents. Thus by suitable choice of the composition and positioning of the individual panels, separations can be enhanced or condensed at will.

A combination of these two modes of operation also has useful properties. By choice of a suitable mobile solvent it is possible to separate the pesticides from co-extractives by development along a silica gel panel. By turning the plate through 90 degrees and developing in a more polar solvent on to an alumina panel, mixtures of pesticides can be separated in a clean state.

Gradient-layer chromatography

A novel variant of the "moving-spreader" layer applicator has been introduced by Stahl (38). With this apparatus it is possible to prepare layers of uniform thickness which are graded from pure adsorbent A at one side to pure adsorbent B at the other, intermediate zones consisting of varying mixtures of the two materials with a 1:1 composition in the centre. By developing the chromatoplate from reagent A to reagent B, separations may be enhanced or minimized according to which adsorbent is the more active. In this way its action is somewhat similar to a bipartite multiband-plate prepared as described above, although it shows considerably less versatility in that only two adsorbents are used. However, its main use would appear to be as a research tool in investigating the retention characteristics of mixtures of two adsorbents in varying

ratio, by applying a series of spots of the material under examination across the plate from reagent A to reagent B and developing in such a way that each spot migrates along a lane of constant composition. By examination of such chromatograms a suitable admixture may be chosen which will effect the desired separation.

Preparation and application of sample extract

Extraction and clean-up

Thin-layer chromatographic procedures are, in general, much more tolerant of co-extracted materials than are paper or gas-liquid chromatographic systems. The intrinsic clean-up properties of the layer materials most frequently employed, silica gel and alumina, render minimal the amount of purification of the extract required. Morley and Chiba (39) have proposed a method for the direct thin-layer chromatography of organo-chlorine pesticide residues in some plant extracts without prior clean-up, samples showing possible pesticide content then being further examined by gas-liquid chromatography. This system simplifies the procedure greatly, eliminates some possible sources of pesticidal loss and extraneous contamination, and allows the rapid screening of a large number of samples. Unfortunately its application is rather limited although the introduction of an acetonitrile-hexane partition procedure as a clean-up improved the chromatoplate's background and allowed the method to be used for a wider range of compounds.

For samples of vegetable origin, the extraction and clean-up procedure of Goodwin, Goulden and Reynolds (40) is often suitable when organo-chlorine pesticides are under examination. Extraction with acetone followed by partition into hexane, after adding sodium sulphate solution, yields a solution sufficiently clean for gas-liquid or paper chromatography and well suited for application to a thin-layer chromatoplate. When examining samples of waxy vegetables or ripe fruit in this way, the extracts are not suitable for the former two techniques but may still be used for thin-layer chromatography. Organo-phosphorus pesticide residues may be suitably extracted from vegetable tissue with a mixture of ethyl methyl ketone and hexane $(3 + 2^V/_v)$ (41). Dinitrophenol herbicides have similarly been extracted with ethyl methyl ketone : ether, $3 + 2$ (36).

For the efficient extraction of pesticides from fatty materials a solvent such as hexane is essential. This, of course, also dissolves a considerable amount of the fat and although thin-layer chromatography is fairly tolerant of vegetable co-extractives, fatty or waxy materials may affect

the observed R_F value of the chromatographed pesticide; usually a reduction of this value is noticed. Organo-chlorine pesticide residues after extraction from animal produce have been cleaned-up for gas-liquid chromatographic examination by means of a dimethylformamide (DMF) partition process, followed by passage through an alumina or magnesia column (42). A similar clean-up process is suitable for thin-layer chromatographic purposes but the columnar clean-up stage may usually be omitted. Similar partition processes using acetonitrile (43) and dimethylsulphoxide (44) have also been used for this purpose.

In general it is the total load of material that is to be applied to the chromatoplate at one point that governs the thickness of the layer required for efficient chromatographic clean-up. For clean extracts the usual layer thickness of about 250μ is adequate; for preparative and clean-up purposes 500μ or 1 mm thickness is more usual as previously described. The amount of previous clean-up required may therefore be related, in part, to the availability of spreading apparatus capable of producing layers of various thickness.

Application of the sample extract

In order to obtain accurate and reproducible thin-layer chromatograms a few simple rules must be observed during the application of the sample extract to the adsorbent layer. The nature of the solvent used for the final solution of the extract to be applied to the plate is very important. In order to ensure that the size of the spots shall be as compact as possible, the chosen solvent should be of as low a polarity as is consistent with good solubility of the pesticide. This is particularly important when only very dilute solutions are available, when it may be necessary to apply the extract repeatedly to one spot in order to ensure sufficient material for clear visualization. Such "over-spotting" is liable to induce radial chromatography at the origin when polar solvents are involved. The solvent should also be readily volatile yet not of so low a boiling point that standard solutions cannot be maintained in constant concentration or that evaporation, with consequent deposition of the dissolved material, occurs while within the applicator. Solvents with boiling points in the range 40–60°C are usually preferred whenever possible.

The sample solution may be applied to the layer surface by gently touching it with a filled calibrated capillary or micro-pipette or by means of a micro-syringe of suitable capacity; volumes of the order of 1 to 5 μl per spot are preferred. To aid in the accurate alignment of a series of

spots across the chromatoplate, a suitably drilled template, usually constructed of a transparent plastic material, is often used both as a guide and to protect the surface of the layer. The line of spots so applied should be about 15 to 20 mm from one edge of the carrier plate and parallel to it, individual spots being at least 1 cm apart. The line should also be perpendicular to the direction of spreading to avoid possible unevenness in thickness across the layer. Care must be taken not to penetrate the layer with the tip of the applicator or irregular shaped spots are liable to result on developing the chromatogram (45). In order to maintain the desired compactness (<0.5 cm) of the origin spots, Mangold (27) advised the use of a stream of nitrogen to ensure rapid evaporation of the solvent from the plate, while Miller and Kirchner (46) employed a low temperature hot-plate for the same purpose.

Ritter and Meyer (47) have mechanized the operation of spotting the samples on to the layer. They designed a syringe which traverses the chromatoplate, applying controlled doses of the solution as required; a similar "streak" applicator was used by Coleman (48). Morgan (49) produced a multiple capillary device for the simultaneous application of many solutions to a single chromatoplate; Bark *et al* (50) found that such rapid spotting techniques improved R_F reproducibility. As alternative modes of spotting, Metz (51) has used a system of elution from a filter paper triangle, while Tate and Bishop (52) described the use of a wire loop such as is employed for bacteriological purposes.

Although the application of circular spots is most often recommended, Honegger (53) advocated that the sample should be applied as a thin band, about 1 cm long. Techniques of this nature are especially suitable for extracts of residues which have not undergone a very thorough clean-up process and in which the ratio of co-extractives to residue is rather high. The load of material which may be successfully applied to the chromatoplate is limited by the layer thickness on one hand and by the sensitivity of the visualization system on the other. Generally speaking, amounts of material in the range 0.5 to 10 μg may be chromatographed on 250μ thick layers to give clearly defined regular spots with little or no streaking. Where large amounts are encountered it is advisable to dilute the extract further and to repeat the chromatogram. Variable R_F values have been observed where overloading of the adsorptive capacity of the layer has occurred (54). In the case of purely preparative thin-layer chromatography, however, this factor is frequently less important than in diagnostic work and large loads may then be safely used.

Development techniques

Thin-layer chromatoplates are normally developed by means of an ascending mobile solvent, the plate being held in an approximately vertical position. Descending – solvent chromatographic techniques are reserved for the separation of substances of low R_F values, extended runs being obtained by allowing excess solvent to drip from the bottom of the chromatoplate (55). Horizontal development may also be used but since a wick of some sort is required to maintain the supply of the mobile solvent, this mode is somewhat more difficult to apply.

There are many factors governing the successful development of a thin-layer chromatoplate. To ensure even running of the solvent front it is advisable to remove adsorbent from both side edges of the plate, leaving about 5 mm of clear carrier plate. If many samples are spotted closely across the plate it may also be necessary to rule channels between each pair of adjacent spots in order to ensure that no cross contamination can occur should a sample contain an unduly large amount of residue.

The mobile phase chosen for the development will depend upon the nature of separation required, and also upon the activity of the adsorbent material. When dealing with a new or unknown compound, preliminary tests should be made using an active adsorbent together with a non-polar solvent such as hexane. Successive small proportions of a polar solvent may then be added as necessary to obtain the required R_F value or degree of resolution if a mixture is being studied. Microscope slides bearing layers produced by a spray technique are very suitable for tests of this nature.

Development by the ascending-solvent technique is obtained by placing the prepared chromatoplate bearing the sample spots into a tank containing the chosen solvent in such a way that the origin line is parallel to the solvent surface and about 1 cm above it, i.e. a depth of immersion of about 0.5 to 1 cm is obtained. The tank should be sealed by some suitable means, a well-fitting ground glass cover being frequently employed. Development is then usually allowed to proceed at ambient temperature until the solvent front has traversed a fixed distance or has taken a certain time. It is frequently recommended that the tank should be lined with filter paper dipping into the mobile solvent and should be left to stand for at least one hour before inserting the chromatoplate. Lining the tank in this way serves to ensure that the solvent and its vapour quickly reach equilibrium within the confines of the chamber, a state which assists in maintaining a level solvent front across the layer (14).

An often-overlooked factor in thin-layer chromatography is that of the volume of the development chamber.   Tanks supplied with the various types of commercial spreading apparatus are usually only slightly larger than the standard 20×20 cm carrier plate and about 5 to 10 cm wide. Paper chromatographic development chambers are usually rather larger than this and since they are already available in most pesticide residue analytical laboratories, their conversion to thin-layer use has frequently occurred.   Whichever size of tank is chosen it must be closely adhered to for all accurate comparative work.   Provided that known standard pesticides are spotted on to every plate and that confirmation of identity is all that is required, small variations in tank-volume will be relatively unimportant.

The humidity of the atmosphere within the development chamber has been found to have a profound influence on the separation of some 2, 4-dinitrophenyl-hydrazones (20).   In the absence of water vapour excellent resolution of six compounds was obtained, while all substances migrated with the solvent front when atmospheric moisture was not excluded.   In order to obtain such satisfactory separations it was necessary to devise a tank through which dry nitrogen could be circulated prior to allowing the mobile solvent to contact the chromatoplate.   This apparatus was similarly found useful for preventing oxidation effects during the chromatography of methyl esters of some unsaturated fatty acids.   Geiss and Schlitt (56) have also shown the variation of R_F value of polyphenyl hydrocarbons which could be induced by large changes in the relative humidity of the development chamber atmosphere.

Differing views have been expressed in the literature as to the extent of the effect of variations in the temperature at which development proceeds upon the R_F values observed on thin-layer chromatoplates.   Stahl (10), studying essential oils on silica gel chromatoplates developed in a hexane-acetic acid mixture, found no alteration in running time on changing the temperatures from 20° to either 4° or 28°C.   The effects of insecure closure of the tank and variation in the depth of immersion of the layer in the mobile solvent were found to be more important.   Brenner *et al* (57) similarly found that raising the temperature of development from 18° to 38°C had virtually no effect on the R_F values of a number of amino-acids developed with a phenol-water mixture, although the reproducibility of these values became poorer.

Muller and Honerlagen (58), on the other hand, in their study of the thin-layer chromatography of cinchona bark alkaloids developed with a

mixture of kerosene-diethylamine-acetone as mobile solvent, found that the observed R_F values were strongly temperature dependent; they advised the use of a controlled 25°C as being most convenient and suitable for their purpose. Similar effects were described by Harthon (59) who advised the inclusion of a reference compound on each chromatoplate to act as a check against variations in R_F value due to temperature fluctuation. Use of the effect of temperature on R_F value has been made by Malins and Mangold (60) in their separation of palmitic and oleic acids on silica gel chromatoplates developed at 4–6°C, these compounds being unresolved at normal ambient temperatures. Stahl (38) has recently devised a chamber for isothermal operation at temperatures ranging from −50° to + 50°C. Development at low temperatures allows the use of low boiling solvents as mobile phase and also renders possible the chromatographic separation of compounds that are appreciably volatile at room temperatures. His results indicate that the effect of variation of temperature on R_F value is more dependent on the nature of the mobile solvent than upon the material under investigation.

The procedures described above relate in general to a single linear development in one direction. Thin-layer chromatography is also suitable for two-dimensional separations, either by means of different mobile solvents in directions perpendicular to one another (61), or by a combination of normal solvent development with an electrophoretic separation (62). Multiple or step development techniques may also be applied, either by repeated application of the same solvent (63) or by sequential use of different solvents (64,65). Gradient elution techniques, whereby the polarity of the mobile solvent is continually changed while the development proceeds, have also been used, suitable apparatus having been described by Rybicka (66).

Visualization of residues

The application of a visualization reagent is usually required before the developed chromatogram may be properly observed. Most reagents suitable for paper chromatographic indication purposes may similarly be applied to thin-layer chromatograms. Additionally, corrosive reagents and elevated temperatures may be used where necessary. Visualization agents fall readily into two classes, general or universal reagents and specific or semi-specific indicators. The reagent is usually applied in the form of a spray; for the best results the droplet size must be very small and also uniform, the reagent must be evenly applied and only the minimum

quantity required to produce the desired effect should be used.   In order
to retain the compactness of the located spot, and hence conserve sensi-
tivity, the compound sought should not be soluble in the solvent used for
the spray and should not form soluble complexes with the reagent.   It is
usual to remove as much as possible of the mobile solvent before spraying
the developed chromatoplate with the visualization reagent.   However,
it is preferable to spray loose-layer chromatograms while they are still wet
with mobile phase which acts as a binding agent and prevents the dispersal
of the layer materials by the mechanical force of the spray.   Some visuali-
zation agents may be incorporated in the layer-mix when spreading the
plates, fluorescent compounds in particular may be used in this way.
Sometimes, however, such "built-in" indicators interfere with the normal
development of the chromatogram.

Sulphuric acid may be used either alone (67) or in combination with
other compounds, such as nitric acid (5), sodium dichromate (68), potassium
permanganate (69) or vanillin (12).   Following such acid sprays it is usual
to heat the treated plate to 100–200°C, various colour changes frequently
being observed (27) which aid in the identification of the compounds under
examination.   Beroza (70) sprayed with sulphuric acid containing either
chromotropic acid or furfural during a study of pyrethroids synergists.
Although it is not usual to use starch-bound chromatoplates when sulphuric
acid is included in the spray reagent, Yamamura and Niwaguchi (71) made
use of such a combination when investigating the separation of aldrin,
dieldrin, endrin and endosulfan.   Alkaline potassium permanganate was
found to be preferable to sulphuric acid for the location of pesticides of
the aldrin-dieldrin type (72).

Other reagents of general applicability include antimony trichloride or
pentachloride (11), iodine (60) and various fluorescent compounds, the
latter being frequently used together with a bromine vapour treatment.
In the pesticide field the above-mentioned antimony chlorides have been
used to locate pyrethroids (61) and chlorophenoxyacid esters (63).   Iodine
vapour has been used as a general visualization indicator by Conkin (73);
the appearance of the brown spots is reversible and the located compound
is unaffected by the reagent, a useful attribute if the material is required
for further study.   Walker and Beroza (74) list the limits of detection for
62 pesticides and associated compounds located by exposure to iodine
vapour for five minutes; the values quoted range from 0.1 to 5 µg
with an average of about 1.5 µg.   Iodine vapour has also been used by
Stammbach *et al* (75) for phenkapton and its commercial impurities, by

Chiba and Morley (76) in a study of carbaryl, and by Katz (77) for locating DDE and dichlorobenzophenone.

Fluorescent compounds have enjoyed wider popularity among pesticide residue analysts, the spots usually being located and marked by observing the quenching effect of the compound on the background fluorescence when viewed under UV light. Kirchner *et al* (9) used zinc-cadmium sulphide as a built-in phosphor to indicate the presence of biphenyl on their chromatostrips. Fluorescein, either built-in or spray-applied, has been used by Spickett (78) for pyrethroids and by Salo *et al* (79) for organo-phosphorus pesticides, exposure to bromine vapour showing the yellow spots on a red background, Walker and Beroza (74) added silver nitrate to this fluorescein-bromine combination and give limits of detection ranging from 0.5 to 10 µg for 59 pesticidal compounds; for the organochlorine compounds 7 min irradiation with UV light was also required. Dichloro-fluorescein has been found useful for organo-phosphorus pesticides (34). Some esters of MCPA and mecoprop have been located by means of Rhodamine B (63).

Among the more specific visualization agents two have been widely used. Palladous chloride has been found preferable for organo-phosphorus compounds by Bäumler and Rippstein (30), Blinn (80) and Steller and Curry (81). Silver nitrate, with UV irradiation, has been most popular for chlorine-containing pesticides. The "chromogenic reagent" of Mitchell (82), i.e. silver nitrate with 2-phenoxyethanol, has been universally used for visualizing paper chromatograms (18,74) and has been widely adopted for similar purposes on thin-layers. On silica gel or alumina plates, however, it is not very satisfactory because dark backgrounds are obtained which limit its sensitivity. A simple 0.5% ethanolic solution of silver nitrate has been found to be more satisfactory (83). Other variations on this theme include ammoniacal silver nitrate (39,84), ethanolamine or potassium hydroxide with silver nitrate (72), silver nitrate-formaldehyde-potassium hydroxide (79), and silver nitrate-nitric acid (63).

Abbott, Egan and Thomson (85) have described spray reagents consisting of a combination of silver nitrate with one of several pH indicator compounds. Bromophenol blue gave yellow spots on a blue background with organo-chlorine pesticides without irradiation with UV light. Bromo-cresol green also showed promise but required irradiation and further heating for the best results. Plates containing built-in silver nitrate are suitable for the detection of organo-chlorine pesticides, although a rather "grainy" background may be obtained. For organo-phosphorus com-

pounds, however, such plates are quite unsuitable as considerable streaking of the pesticide occurs. One benefit given by the use of silver nitrate-UV irradiation as an indicator system is that since only a very small amount ($<10\%$) of the pesticide is affected by the irradiation, the bulk may be extracted for examination by other means (34). These workers have also studied the properties of a number of other indicator compounds, belonging in the main to the azo and triphenylmethane classes of dyestuffs, when applied as visualization agents for pesticidal compounds. Brilliant green (colour index No. 42040) showed very useful reactions and good sensitivity. With the aid of this material it is possible to locate organo-chlorine, organo-phosphorus and triazine compounds and to distinguish between them. On spraying the silica gel chromatoplate with an 0.5% solution of brilliant green in acetone, organo-chlorine pesticides are observed as pale yellow spots on a green background and may be readily marked. On placing the sprayed plate into an atmosphere of bromine vapour (the plate must still be damp with acetone) the green background and the spots of organo-chlorine pesticide disappear but triazine herbicides are located as semi-transient green spots on white and organo-phosphorus pesticides appear as permanent dark green or yellow spots.

Among the specific visualization methods mention must be made of the use of esterase inhibition procedures for the detection of organo-phosphorus compounds and their metabolites. The sensitivity of this procedure varies very markedly with the compound studied, for example the anti-cholinesterase activity of phorate oxygen analogue sulphone is one thousand times that of the parent phorate and its limit of detection is correspondingly lower. Methods used on paper chromatograms (86,87) have been similarly applied to thin-layer separations (88). The developed paper or plate is briefly exposed to bromine vapour and placed in contact with a sheet of filter paper which has been impregnated with out-dated human plasma. After incubation for 10 to 20 min at 35 to 40°C the paper is removed and sprayed with acetylcholine bromide and bromothymol blue or bromophenol blue. After a short while (5–10 min) the transferred spots appear in blue on the yellow background. Using techniques of this nature sensitivities down to about 10 ng have been obtained from developed thin-layer chromatograms.

The documentation of chromatograms

As thin-layer chromatography increased in importance and widened

in scope, the need for a documentation system became recognized. The number and variety of suggested systems implies that this is not an easy matter. This is one field in which paper chromatography usually scores over thin-layer procedures; the filter papers are readily marked, should the spots be transient, and can be stored almost indefinitely for future reference as required. The fragile nature of the layer of material, however, and the relative expense of carrier plates makes prolonged storage of thin-layer chromatoplates impractical and uneconomic. Published methods for preserving or recording thin-layer chromatograms can be divided into four main classes:—(i) Preservation of the layer; (ii) simple tracing processes; (iii) photographs or photocopies; (iv) direct documentation on to sensitized papers.

Meinard and Hall (4) preserved their chromatograms by applying a length of transparent adhesive tape to the layer in such a way that the two ends were free for notebook mounting while the layer surface bearing the located spots adhered to the tape. Complete chromatoplates were also protected by covering them with a film of transparent material. For the fixation and preservation of loose-layer chromatograms, Mottier and Potterat (89) employed impregnation with paraffin wax or cetyl alcohol at 104°C; spraying with collodion (90) or polyvinylacetate was found to be successful only in fixing the surface of the layers. For bound-layers on plastic plates, Squibb (17) used a spray of *Tuffilm No. 543* which gave the surface an acetate-film finish and enabled the plates to be sliced into strips for radioactivity counting purposes. Lichtenberger (91) found that a spray of a polyvinylpropionate solution could be used to fix the layer material together in such a way that the entire chromatogram could be peeled off the plate or floated off after a short immersion in water. Similar sprays are available commercially (*Neatan*, E. Merck and Co.), but in our hands only limited success has been achieved, fragmentation readily occurring.

The use of tracing paper or cloth (8,92) to document chromatograms has the benefit of simplicity, but manual processes of this nature can only yield an approximate representation and the rather soft nature of the layer surface makes the procedure somewhat indecisive. Similarly a copy-drawing (11), of the plate, while adequate for the reproduction of the observed colours of spots and their relative position, is unlikely to yield an accurate document in terms of R_F value, size of spots, etc.

Photography, in black and white or in colour, has been widely used for the production of copies or slides for projection (8,11). Brown and

Benjamin (68) recommend illuminating the chromatograms by transmitted as well as by reflected light in order to obtain the clearest representation by photographic means.   Such methods, however, require expensive apparatus and experienced workers if true records are required; the time involved in processing the developed film and preparing prints is comparatively long and the process is wasteful if only one or two copies are required at a time. Since some visualization agents rapidly fade, the camera must always be available when required and therefore cannot be put to other use.

Commercial automatic copying machines have also been brought into use for documentation purposes.   Getz and Lawson (93) found the "Photo-rapid" diffuse transfer process suitable and Hilton and Hall (94) made use of a "Xerox 914" office copier to obtain positive replicas of thin-layer chromatograms in about 30 sec.   Once again these machines are costly and can hardly be justified for the purpose of copying chromatograms alone, although where they are available they may be put to good use.

The direct use of photosensitive papers provides a rapid and inexpensive way of documentation. Gordon (95) described a method for recording uv-absorbing spots on paper chromatograms by ferric ferricyanide blue-print paper, development with water being required; Zeitman (96) also used a blueprint process.   Photographic contact paper was similarly used by Abelson (97) for thin-layer plates.   Activated zinc oxide papers were used by Sprenger (98) together with a triboluminescent compound, but darkroom facilities are essential.   The use of diazo dry process papers, as suggested by Eisenberg (99), offered a simple method.   A combination of photoflood illumination with pre-ringing of the developed spots (85) has reduced the elapsed time required from over 10 min to less than 1 min. In view of its simplicity and wide applicability the procedure is described here in some detail.

Diazo or ammonia process papers are, in general, insensitive to normal levels of illumination and can therefore be freely handled under ordinary laboratory lighting conditions.   Papers of various degrees of sensitivity are available, the fastest papers giving the best contrast.   When intense light falls on the paper, the diazo-compound is destroyed and can there-fore no longer couple with the built-in coupling agent on exposure to ammonia vapour.   Where the light has not fallen, coupling occurs and coloration quickly appears; blue, black and red papers are widely available. "Ammonax" 8.M13 Positive Diazo Paper (Hall-Harding Ltd., London) is a very sensitive blue paper and "Densblack" Ammonia Process Paper, type 45, 9x (E. Mason and Sons, Ltd., Colchester) is a black paper giving

very good contrast and definition. Either positive or negative copies can be obtained on these papers and the process is equally suitable for copying paper chromatograms, graphs, typescripts, etc., although longer exposures are required.

To copy a chromatoplate, either circumscribe the spots with a soft-lead pencil or scrape them completely from the plate. Similarly mark the origin points and the solvent front; any other information may also be inscribed on the layer, writing letters backwards and from right to left. Remove excised material by gently blowing and place the marked plate face downward on the sensitized surface of a sheet of the diazo-paper; $10 \times 8''$ is a convenient size when using 20×20 cm chromatoplates. Illuminate from above with four 275w photoflood lamps mounted in a reflector ($25 \times 25 \times 20$ cm) placed centrally over the plate. After exposing for from 5 to 15 sec, depending on the speed of the paper, remove the light source and suspend the paper in an atmosphere of ammonia. The marked spots appear almost immediately as white rings or spots on a coloured background. The copies so obtained are permanent, readily filed for later inspection and may be inscribed as desired.

Quantitative evaluation of chromatograms

The techniques which have been applied to the quantitative evaluation of thin-layer chromatograms fall readily into two classes. That which has the largest following among pesticide residue analysts comprises those procedures in which the chromatographed compound is separated from the layer absorbent before the application of standard micro-chemical analytical methods such as spectrophotometry, gas-liquid chromatography, etc. The alternate technique involves the relationships which exist between the weight of compound contained in the located spot and its size, density of coloration (visual or photometric), or radioactivity.

The very small amounts (micrograms) of material usually applied to a thin-layer plate precludes the use of simple weighing of the eluted compound unless many chromatoplates are developed and the products combined (100). Spectrophotometry in the visible and uv regions of the spectrum can readily be carried out with the weights of material (0–10 μg) which may be eluted from a single spot on a chromatoplate. Kirchner *et al* (9) used uv spectrophotometry to determine diphenyl eluted from silica gel; Deters (101) has similarly determined traces of pentachlorophenol. With these techniques some interference may be observed from extraneous material contained in the absorbent layer. Pre-extraction with

methanol has been found (102) to reduce this interference, but the preparation of a blank extract of an adjacent area of the layer was still necessary for full correction; other errors were introduced by incomplete elution from the absorbent. Dimethoate and its oxygen analogue have been determined in vegetable tissue by Steller and Curry (81) who digested the eluted pesticides with a nitric-perchloric acid mixture and evaluated the liberated phosphorus by a molybdenum blue spectrophotometric procedure. Dinoseb has been determined spectrophotometrically as its sodium salt after a clean-up on wedge-layer plates (36).

Infra-red spectrometry has also been used for the quantitative determination of organo-phosphorus pesticides (34) as well as simultaneously providing conclusive evidence of the identity of the separated pesticide. Gas-liquid chromatography provides a very convenient method for the determination and further clean-up of the eluted pesticide spots. The use of electron-capture detection for both organo-chlorine and organo-phosphorus compounds (41,103) gives very great sensitivity. The use of a silver nitrate-uv irradiation procedure for the visualization of the chromatogram leaves the bulk of the pesticide unaffected in each spot since only the surface of the layer comes under the influence of the irradiation. Thus elution of the pesticide from the treated chromato-plate with dichloromethane gives ample material for an approximately quantitative evaluation. If insufficient material is present to give a visible spot with the visualization reagent used, then elution of that area of the layer suspected of containing the pesticide may give sufficient material for further examination by gas-liquid chromatography.

Biological assay, using *Drosophila melanogaster,* has been used by Salo *et al* (79) to determine some organo-chlorine and organo-phosphorus pesticides separated on silica gel containing built-in fluorescein as indicator. Marco and Jaworski (104) utilized C^{14}- labelled Colep for the determination of residues of the pesticide and its various metabolites by radiometry. A suitable scanner for thin-layer chromatography has been described by Wilde (105).

A useful description of the sequence of techniques involved in the routine quantitative analysis of materials which have been separated by thin-layer chromatography has been given by Millett, Moore and Seaman (106). Application of the samples, removal of the layer material bearing the located compound, and the elution of the latter from the absorbent are detailed; the accuracy and precision (1–2%) of the techniques are also discussed.

The second class of methods used for the quantitative evaluation of thin-layer chromatograms follows more closely those techniques which have been well established in the field of paper chromatography (107). Spot density measurements have been used by Privett and Blank (108) in the determination of component triglycerides. The areas under the densitometer curves were found to be directly proportional to the amount of sample applied for the saturated triglycerides and glyceryl residues of the unsaturated glycerides, spots being located by charring with 50% sulphuric acid. However, the area given varied with the type of structure of the compound. Squibb (109) made densitometric measurements on amino-acids located with ninhydrin and found a coefficient of variation of $\pm$ 6.9%. Reflectance densitometry as used for the paper chromatographic determination of herbicides (83) has been found to be less successful with thin-layer chromatograms of similar compounds, largely owing to the fragile nature of the layer surface and the difficulty in obtaining a sufficiently clean and uniform background with the silver nitrate reagent used. A review of photometric methods has been given by Klaus (110).

Methods based upon the measurement of spot area avoid the difficulties associated with elution of the material from the absorbent and the possibilities of further pollution of the purified sample. Seher (111) simultaneously chromatographed samples of the unknown and a series of standards applied to the chromatoplate in equal volumes of solution. After rendering the developed chromatogram visible, the areas occupied by the standard sample spots were determined and plotted against the corresponding weight of material. Reference of the area of the unknown sample spot to this curve gave a measure of the material present. Purdy and Truter (112) showed that the square root of the area of the spot is a linear function of the logarithm of the weight of the material it contains. Statistical evaluation (113) showed that this relationship was preferable to those of area against logarithm of the weight or logarithm of the area against logarithm of the weight. Planimetric means were used by Aurenge *et al* (114) to determine spot areas; graphs of area squared against weight of material were linear. They also traced the chromatograms, cut out the traced spots and weighed them in order to determine the area of the spot more accurately, the weight per cm^2 of the tracing paper being known.

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Table I gives a few examples of the wide variety of chemical substances whose separation, purification and identification have been effected by the use of thin-layer chromatographic techniques.

Table I

Thin-layer chromatographic separations

Class of Compound	Adsorbent	Mobile phase	Visualization agent	Reference
Alkaloids	Silica gel	Chloroform, diethylamine (90 + 10)	Iodoplatinate	115
Antibiotics	Silica gel	Acetone, methanol (50 + 80)	Iodine azide	116
Antioxidants	Silica gel	Chloroform	Phosphomolybolic acid	117
Fatty acids	Silica gel	Petroleum ether, diethyl ether (90 + 10)	Sulphuric acid	118
Food dyes	Cellulose	n-Propanol, ethyl acetate, water, (60 + 10 + 30)	Self indicating	119
Pesticides				
(A) Organo-chlorine	Silica gel	Hexane	Silver nitrate	85
(B) Organo-phosphorus	Silica gel	Hexane, acetone (90 + 10)	Brilliant green and bromine	34
(C) Herbicide	Silica gel, kieselguhr (40 + 60)	Cyclohexane, benzene, acetic acid, liquid paraffin (20 + 3 + 2 + 1)	Silver nitrate	83
Plasticizers	Silica gel	Benzene, ethyl acetate (45 + 5)	Fluorescence	120
Sterols	Silica gel	Benzene, ethyl acetate (90 + 10)	Phosphoric acid	121
Sugars	Alumina, silica gel (1 + 1)	Butanol, acetic acid, methanol (20 + 20 + 60)	Aniline phthalate	122
Vitamins	Alumina	Benzene	o-Toluidine + KI	123

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DISCUSSION

DR. M. R. W. BROWN: Could you tell me if you have any experience of using thin-layer chromatography to separate sugars that are normally quite difficult to separate [*Table I*]?

DR. THOMSON: No. The literature, however, has many references to such separation. By preparing multi-band plates it should be possible, by varying the polarity of the layers, to separate even very closely related sugars.

DR. A. R. ROGERS: You have referred to the work of Truter (112) and others, on relating some function of the size of the spot to some function of the weight of material. This seems a counterpart to biological assays. Do you agree that there is no unique answer?

DR. THOMSON: I agree that this relationship ought to be developed for each system. If, from the developed plate, the relationship of the square root of the area and the weight of compound applied to the plate is to be a straight line, then it is essential that the same quantity of the compound should be applied to the plate in the same volume of solvent. With care and practice it is possible to get a straight line relationship down to very small quantities, i.e. 0.5 μg.

DR. A. R. ROGERS: Could you tell us of your experience with Kodak plastic plates?

DR. THOMSON: We did not find these plates of any particular use in pesticide residue analysis where the plates were developed in hexane:acetone mixtures. However, other people might find them useful for the separation of other substances using different solvent systems.

MR. J. D. CHESHIRE: I have heard that the simplest and cheapest plate is made from reeded or fluted glass. One pours the silica gel slowly over this and then smoothes it off with a glass rod; after drying one applies one spot to each flute. Do you have any experience of this?

DR. THOMSON: Fluted glass has been used for a considerable time. The slurry is poured on to the fluted glass and a straight edge drawn over the top produces an excellent thin-layer plate subdivided into several sections. Another use of fluted glass is for the preparation of loose-layers. Any suitable-sized powder can be used in place of the normal slurry and a loose-layer plate produced. It is essential that such a plate be developed at an angle not exceeding 15°. However, whereas bound-layer chromatoplates develop in 30 to 35 min, loose-layer chromatoplates only require 4 to 5 min for development. The disadvantage of loose-layer chromatography on fluted glass is that the variable thickness layer gives a rather large diffuse spot, and quantitative work, based on a square root of area against log of the weight relationship, is not possible.

MR. C. YOUNG: Do you prewash your own plates, and do you examine your solvents for impurities, especially since you are looking at your plates by ir?

DR. THOMSON: A washed plate is a very useful thing to have when using ir as an end method because any type of chemical impurity in the material will interfere. In Germany, however, Merck produce an extremely pure stationary phase that does not require prewashing.

MR. C. YOUNG: Do you have any experience of variable RF with concentrations?

DR. THOMSON: Generally if you start with a very small amount of material you end up with a precise spot. If you start off with a large amount of material which tends to get spread out anyway on the baseline, you end up with a large spot and your RF's become a little more doubtful.

Society of Cosmetic Chemists of Great Britain

ANNUAL REPORT 1965-66

Membership

The membership of the Society on 31st March 1966 is shown below in comparison with the figures at the same time during the two preceding years:

	1964	1965	1966
Honorary Members	6	6	6
Members	351	359	378
Associates	49	48	48
TOTAL	406	413	432

Scientific Meetings

The highlight of our 1965/66 lecture programme was provided by the second Medal Lecture delivered by Lord Todd of Trumpington on "The Changing Face of Organic Chemistry". Special mention can also be made of the perfumery lecture organised in conjunction with the British Society of Perfumers and which was attended by 95 people.

The other lectures although broader in scope than in previous years attracted responsive audiences. Council wishes to record its thanks to Mr. Norman Van Abbè for organising a most satisfactory lecture programme.

The full programme for last year is detailed below:

Thursday, 7th October 1965

The subjective assessment of the consistency of materials in relation to physical measurements.

G. W. Scott Blair, M.A., D.Sc., F.R.I.C. (National Institute for Research in Dairying).

Thursday, 2nd December 1965

The selection of scientific personnel.

R. Stokes, B.A., M.B.I.M., M.I.P.M. (Glaxo Laboratories Ltd.).

Thursday, 6th January 1966

The economics of research.

C. Freeman, B.Sc. (National Institute of Economic and Social Research).

Thursday, 3rd February 1966

Perfumery Lecture (Jointly with the British Society of Perfumers).
Mr. Jordi-Pey (Firmenich).

Thursday, 3rd March 1966.   MEDAL LECTURE:

The changing face of organic chemistry.

Lord Todd, F.R.S. (Professor of Organic Chemistry, University of Cambridge).

Wednesday, 13th April 1966

Some aspects of laboratory planning.

D. J. Alexander, B.Sc. (Unilever Research Laboratory, Isleworth).

Thursday, 19th May 1966

Film evening.

Symposia

In November 1965, 84 people attended the autumn symposium held at Bristol on the subject of "Physical Methods".   The spring symposium was held at Eastbourne on the subject of "Colour" and was attended by 93 delegates.

The Council wishes to record its appreciation to Mr. N. J. Van Abbè and Mr. S. J. Bush for their part in organising these symposia.

Journal

As the Journal primarily reflects the scientific status of the Society its importance cannot be over-estimated.   The new format of the Journal has been well received, and continued efforts have been made to improve the standard of publication.

Council wishes to record its thanks to the Honorary Editor and his Publication Committee for maintaining the progressive improvement in both journal presentation and content, which has been a feature of previous years.

Committees

1963 saw the formation of a number of committees to administer the increased activity of the Society. During the past year the value of these committees has been fully demonstrated.

Scientific Committees (Chairman: Dr. A. W. Middleton)

Analysis Sub-Committee (Chairman: Mr. S. J. Bush)

The investigations into methods of analysis for hexachlorophene in toilet preparations is now complete. A report on this study will be published very shortly. A preliminary study of methods of determining dyestuffs in products has been made.

Toxicology Sub-Committee (Chairman: Mr. N. J. Van Abbè)

The committee considered draft proposals for the harmonisation of legislation for toilet preparations in common market countries, submitted by Dr. G. Carriere, Central Co-Ordinator for Legislation. Comments on the original and revised proposals were given. At the request of the Spanish Society comments were given on a proposed Spanish Food Code which embraced certain toilet preparations.

Public Relations Committee (Chairman: Mr. A. Herzka)

Increased attention has been given to the scope and quality of material sent to the press and other bodies.

Education Committee (Chairman: Dr. M. Cantley)

Seventeen candidates out of a class of 18 sat for the examination in June 1965; ten were successful and were given the Society's Diploma. One of the candidates in actual fact sat his examination in Ceylon, having been transferred from the U.K. towards the end of the course. The £5 prize was awarded to Miss H. C. Birrell. In September 1965, 23 students were enrolled, which number validates the decision to change to a one-year part-time course.

As Brunel College will eventually be moving to Uxbridge, the 1966-67 Diploma Course will be transferred to the Borough Polytechnic. No substantial changes in the syllabus will be made, but as a target we hope that eventually cosmetic science will be accepted as a topic for L.R.I.C.

The Society's status relating to cosmetic education has been well demonstrated during the year and we were consulted by a number of

bodies on this subject. At present we are in contact with the London College of Fashion who have asked us to advise and to supervise their proposed one-year course aimed at students at 'O' Level, and which will cover certain aspects of cosmetic science. We have also been approached to write a Careers Handbook, which responsibility has been passed to the Education Committee.

Dr. Cantley, his committee and the lecturers have worked very hard in this year of change and increased activity and the Council thanks them most sincerely for their sterling efforts.

Relationship with other Organisations

Toilet Preparations Federation

Relationship with the T.P.F. has been strengthened by the institution of biannual meetings of the principal officers of both bodies, together with frequent informal contact between the general secretaries of both associations.

British Society of Perfumers

The Council of both Societies have agreed to hold an annual meeting between the principal officers to discuss matters of mutual interest. The first meeting will be held in June.

Parliamentary and Scientific Committee

The Society was represented at all the meetings of the Parliamentary and Scientific Committee, and this contact has already proved of considerable value.

I.F.S.C.C.

The Council of the I.F.S.C.C. met in Milan, September 1965. We were represented by Dr. M. Cantley, Mr. J. B. Wilkinson and Prof. A. N. Worden.

The Swedish Society was admitted as a member of the Federation. Education was discussed at some length and we provided full details of our Diploma Course. No general educational policy was agreed, but Dr. Cantley and Mr. Lester Conrad, of the American Society, were appointed as co-ordinators in this context.

Social Activities

A Soirée was held at the School of Pharmacy on Saturday, 9th October 1965. During the evening, Diplomas were presented to successful students of the Diploma examination. Although a social success the numbers both

at this and in the previous year were insufficient to recommend the event as a standing fixture for the future.

The Annual Dinner and Dance was held this year at the Europa Hotel, and was attended by 204 members and guests. Dr. G. Carriere, Central Co-ordinator of all working groups in the I.F.S.C.C., was the Guest of Honour.

Honorary Member

At a Special General Meeting held on 13th April 1966, Mr. Frank Atkins was unanimously elected an Honorary Member of the Society.

Council

The following changes in Council took effect at the 16th Annual General Meeting held on 25th May 1965:

Mr. R. Clark succeeded Mr. A. Herzka as President.

Dr. A. W. Middleton succeeded Mr. R. Clark as Vice-President.

Eight candidates had been nominated for three vacancies on Council, and the following were elected:

Mrs. H. Butler, Mr. C. Pugh, Prof. A. N. Worden.

A complete list of Honorary officers and committees for 1965/66 was contained in the January 1966 *Journal*.

Council met on ten occasions, and all the committees and sub-committees met at frequent intervals.

The following retire from Council after two years' service:

Dr. H. W. Hibbott, Mr. E. K. Clarke, Dr. J. J. Mausner.

Council would like to record their thanks for the service given by these members during their term of office.

Future

The scientific status of the Society hinges on three main activities, namely, the Diploma Course, the *Journal*, and the Scientific Symposia/Lecture programme. Linked to this, our influence and thus our industrial contribution is controlled by the quality of public relations in the widest sense. Finally, our finances critically depend upon the stewardship of the *Journal* and Scientific Symposia.

With these three aspects in mind, the Council and its committees spent considerable time in debating ways of optimising our resources for the future. Council is of the opinion that, as predicted two years ago, the time for us to have permanent office accommodation and a full-time paid secretary is approaching. How best to do this?—next year's Council will have the task of having to provide at least part answer to this question.

As a conclusion, it is evident that the prestige of the Society has increased in the past years through a deliberate outward-looking policy. This must be continued. However, we must also look inwards to our industry and its associated scientifically-linked organisations for new members, who will make a useful contribution to the overall objectives of the Society.

ANNUAL GENERAL MEETING

The Seventeenth Annual General Meeting of the Society took place on the 23rd May, at the Washington Hotel, Curzon Street, London, W.1.

The Annual Report was presented by the President, Mr. R. Clark (*J*.493–498). The Treasurer's Report was presented by the Hon. Treasurer, Mr. R. E. Spate.

Mr. Frank Atkins, B.Sc., F.R.I.C., who had recently been elected to Hon. Membership in recognition of his contribution to the Society, and the cosmetic industry over a long period, was presented with an illuminated scroll.

In the voting for three new Members of Council the following were elected: Mr. N. F. E. Blackmore, Mr. J. M. Blakeway, and Mr. J. S. Cannell.

The officers for 1966-67 are:—

President:	Dr. A. W. Middleton
Immediate Past President:	Mr. R. Clark
Vice-President:	Mr. D. E. Butterfield
Hon. Secretary:	Dr. J. J. Mausner
Hon. Treasurer:	Mr. G. A. C. Pitt
Hon. Editor:	Mr. A. Herzka
Hon. Education Secretary:	Dr. M. Cantley

Mr. L. S. Smith was re-appointed Hon. Auditor, and Messrs. H. W. Fisher & Co. were re-appointed Auditors for the current year.

The business meeting was followed by the customary informal supper.

Mr. R. Clark, retiring President, presenting the scroll of
Honorary Membership to Mr. F. Atkins.

Dr. A. W. Middleton
President 1966-67

1966-67 PROGRAMME

Lectures will be delivered on the following Thursdays:

Venue: The Royal Society of Arts, John Adam Street, London, W.C.2.

Time: 7.30 p.m.

6th October 1966

Modern frontiers in aerosols
H. R. Hearn (Metal Box Company)

1st December 1966

Lucent syrops tinct with cinnamon . . .
Dr. V. L. S. Charley (Beecham Food & Drink Division)

5th January 1967

Group discussion on the subject of the needs and future trends in cosmetic legislation
Dr. R. Allen, Dr. G. Carriere, C. Williams, and Prof. A. N. Worden

2nd February 1967

Cosmetic raw materials '67
W. Harding (Croda Ltd.)

4th May 1967

The examination of hair by new physical techniques
Dr. A. W. Holmes (Unilever Research Laboratory, Isleworth)

MEDAL LECTURE: Wednesday, 22nd March 1967

Professor M. K. Polano, M.D. (Chief Dermatologist, Hague Municipal Hospital, Holland)

1967 DINNER AND DANCE: Saturday, 4th February 1967, at the Europa Hotel, Grosvenor Square, London, W.1.

ANNUAL GENERAL MEETING: Monday, 22nd May 1967, at the Washington Hotel, Curzon Street, London, W.1.

SYMPOSIUM ON PRODUCT TESTING

The Symposium on PRODUCT TESTING will take place in Eastbourne, Sussex, and not in Leamington Spa as previously announced, on 14th and 15th November 1966. Full details will be available at the beginning of August.

MANAGEMENT SEMINAR

A working seminar on THE MANAGEMENT OF LABORATORIES IN CON-SUMER SUPPLY INDUSTRIES, with particular reference to the needs of the cosmetic, toiletry, and allied industries, is to be held in Buxton, Derbys. from 6.00 p.m. Monday, 10th April 1967—6.00 p.m. Thursday, 13th April. For details see *J.* 437.

Further information from Hon. Organiser, 33 Devereux Drive, Watford, Herts., England.

SYMPOSIUM ON PROCESSING AND MANUFACTURING

A Symposium on PROCESSING AND MANUFACTURING will take place in Royal Leamington Spa, Warwicks., on 13th and 14th November 1967. *Programme Secretary:* Dr. J. J. Mausner, Helena Rubinstein Laboratories, Ltd., Central Avenue, West Molesey, Surrey.

DIPLOMA COURSE

The course leading to the Diploma of the Society of Cosmetic Chemists of Great Britain has been held at Brunel College since its foundation in 1957. In view of the revised charter of the college, the next course, which is due to commence on the 19th September 1966, will be held at

BOROUGH POLYTECHNIC,
BOROUGH ROAD,
LONDON, S.E.1.

It is a one-year, part-time day-release course. There are three 3-hour sessions per week, on Monday and Wednesday evenings and Wednesday afternoons, for a total of 32 weeks in the year. The examination, consisting of two 3-hour papers, will be held in June 1967.

The course is the only one of its kind and is designed to give a comprehensive training in all aspects of cosmetic science to persons employed in research or development work in the cosmetic and allied industries. The minimum entry qualification is GCE "A" level, preferably in chemistry, but young graduates will also find it a valuable introduction to industry.

Some of the lectures are from the college and some are from industry. The following topics are covered :

SURFACE CHEMISTRY
SPECTROSCOPY, CHROMATOGRAPHY
PHYSICAL CHEMISTRY (PRACTICAL)
EMULSION THEORY
CHEMISTRY OF OILS, FATS AND WAXES
MICROBIOLOGY
HAIR ; HAIR PRODUCTS
SKIN ; SKIN CREAMS
TEETH ; DENTAL PRODUCTS
PACKAGING
PERFUMERY
LIPSTICKS AND POWDERS

There is accommodation for only 24 students in the course. Enrolment will be at Borough Polytechnic on Wednesday, 14th September, 9.30–12.00, and 17.30–20.00.

IN THE WORLD'S BEST PERFUMES...

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P. ROBERTET & CIE

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