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Journal of the Society of Cosmetic Chemists

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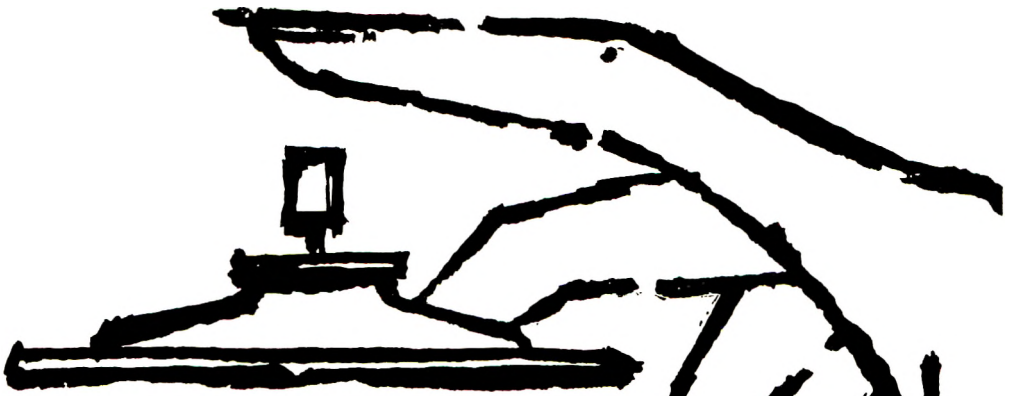

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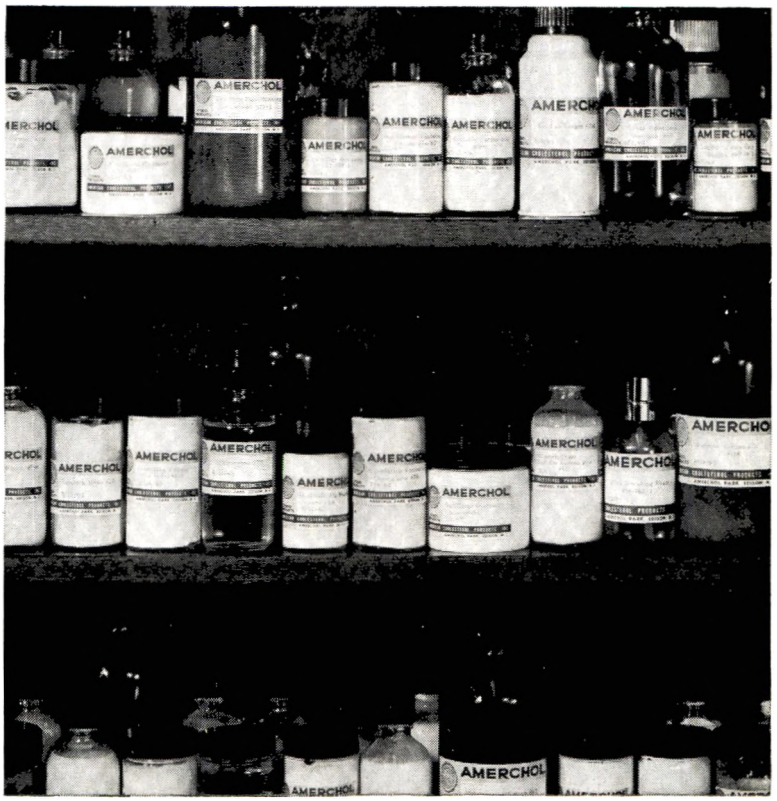

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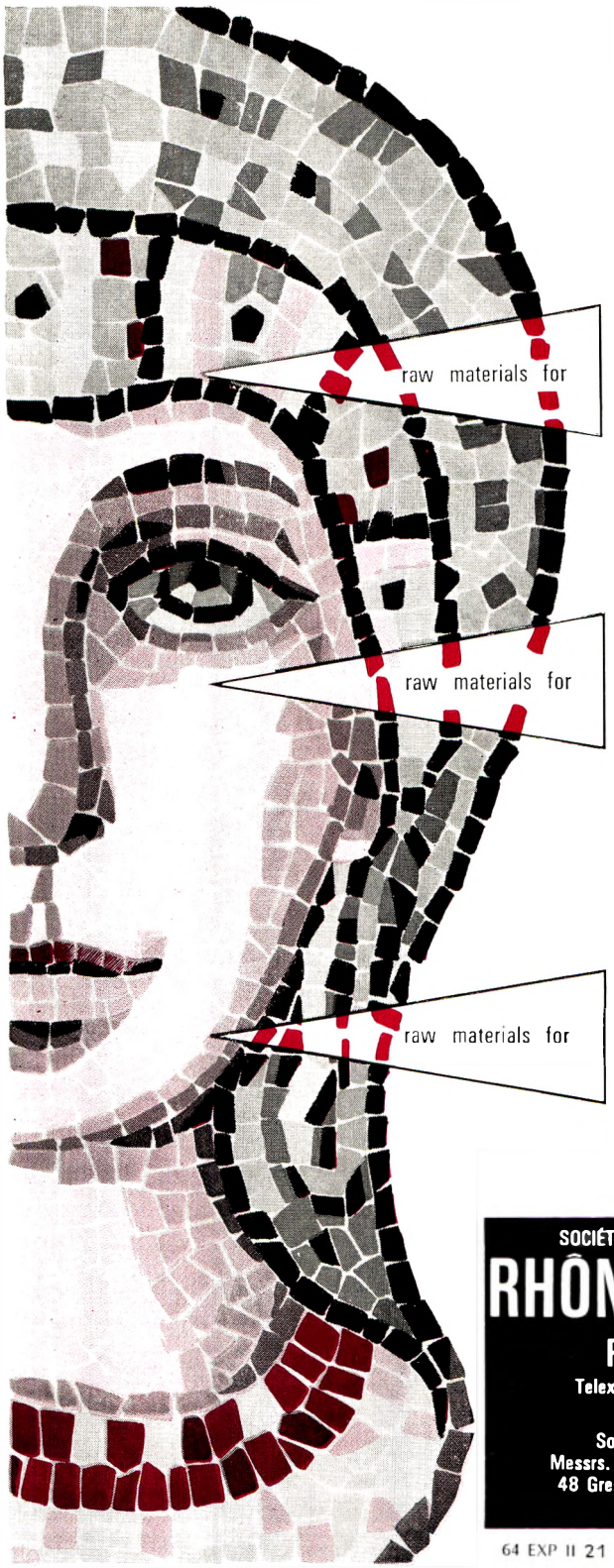

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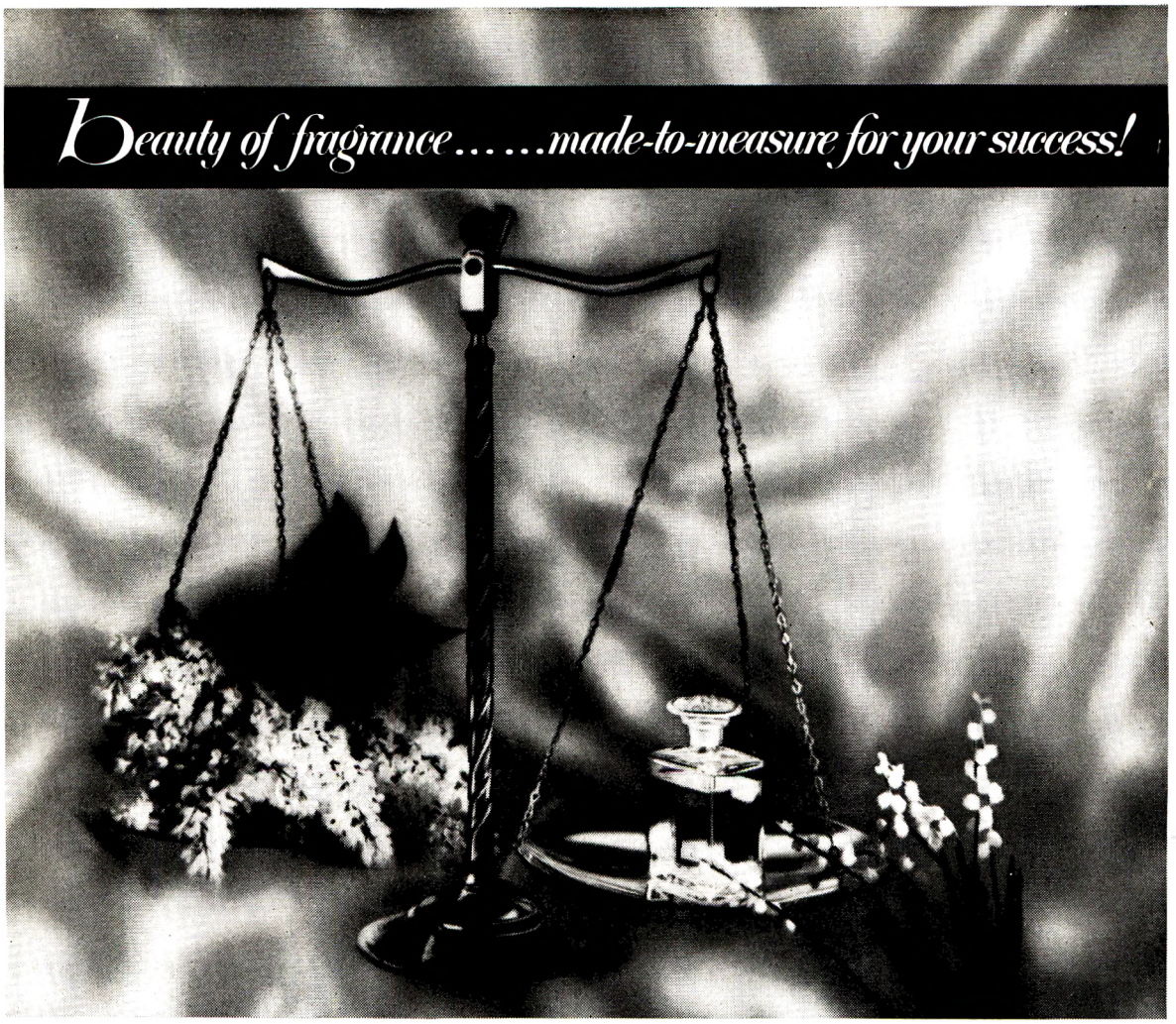

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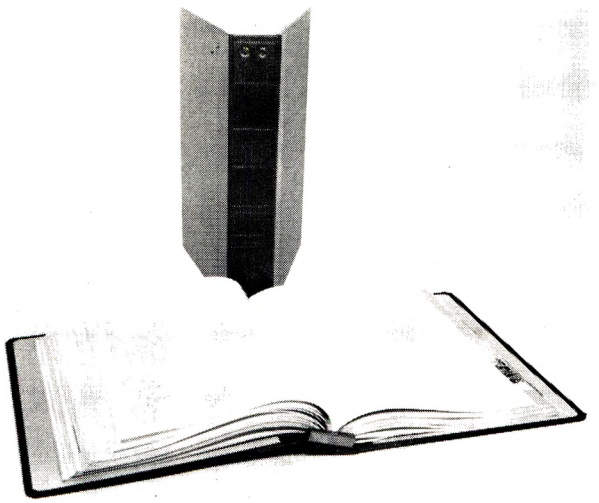

For the convenience of Members who keep their current numbers of the *Journal*, the Society has arranged for a supply of special binding cases to be made available.

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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.

A method for predicting rheological changes in emulsion products when aged: P. SHERMAN. *Journal of the Society of Cosmetic Chemists* **16** 591-606 (1965)

Synopsis—The relationship between viscosity at a given rate of shear and mean globule size is the same for both freshly prepared and aged pseudoplastic emulsions. Consequently the fall in viscosity when an emulsion is aged, due to globule coalescence, can be established from viscosity curves constructed for fresh emulsions of the same composition but with variable mean globule size. The only restriction is that the limits of size distribution should not change too drastically during ageing. The rate constant governing the increase in mean globule size can be determined from simple tests extending over a few days. This enables one to predict what the globule size will be at any future time. In turn the corresponding viscosity can be derived from the viscosity-mean globule size curves. Experimental and theoretical data show good agreement, thus eliminating the necessity to resort to accelerated ageing techniques of questionable value.

Application of attenuated total reflectance IR spectroscopy to toilet articles and household products, 1. Qualitative analysis: N. A. PUTTNAM, S. LEE and B. H. BAXTER.
Journal of the Society of Cosmetic Chemists **16** 607-615 (1965)

Synopsis—The application of IR spectroscopy to the identification of components in toilet articles and household products using a special reflection technique, i.e. Attenuated Total Reflectance, is described. This technique, which is essentially independent of sample thickness, permits spectra to be obtained from bulk samples which are equivalent to those obtained by transmission through thin films. Such a procedure overcomes the experimental difficulties encountered when attempting to study these types of products by transmission spectroscopy.

Examples are quoted of the application of ATR, without any prior sample preparation, to soap-detergent combination bars, toothpastes, washing-up products, all-purpose cleaners, shampoos and bubble baths.

The influence of lanolin derivatives on dispersed systems, 1. The dispersion of pigments in nonaqueous liquids: L. I. CONRAD, H. F. MASO and SHIRLEY A. DERAGON.
Journal of the Society of Cosmetic Chemists **16** 617-636 (1965)

Synopsis—The dispersing activity of several lanolin derivatives is studied by means of modified wet and flow point procedures which are described in detail. Sedimentation tests and microscopic examination are used as supplementary aids. These procedures reveal significant pigment wetting and deflocculating activity for lanolin derivatives when used as additives. The wet and flow point measurements provide quantitative data which can be used to determine efficient additive/pigment ratios for each system studied.

Because of the specific action of the wetting additives no single lanolin derivative can be recommended for all pigment/vehicle systems, but an ideal dispersing aid might utilize a combination of these surface active materials.

Journal of the Society of Cosmetic Chemists

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7	24th June	Great Britain
8	22nd July	Great Britain
9	19th August	U.S.A.
10	16th September	U.S.A.
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J. Soc. Cosmetic Chemists **16** 591-606 (1965)

A method for predicting rheological changes in emulsion products when aged

P. SHERMAN

Presented at the Symposium on "Emulsions", organized by the Society of Cosmetic Chemists of Great Britain at Harrogate, Yorks, on 31st March 1965.

Synopsis—The relationship between viscosity at a given rate of shear and mean globule size is the same for both freshly prepared and aged pseudoplastic emulsions. Consequently the fall in viscosity when an emulsion is aged, due to globule coalescence, can be established from viscosity curves constructed for fresh emulsions of the same composition but with variable mean globule size. The only restriction is that the limits of size distribution should not change too drastically during ageing. The rate constant governing the increase in mean globule size can be determined from simple tests extending over a few days. This enables one to predict what the globule size will be at any future time. In turn the corresponding viscosity can be derived from the viscosity-mean globule size curves. Experimental and theoretical data show good agreement, thus eliminating the necessity to resort to accelerated ageing techniques of questionable value.

Introduction

The rheological properties of cosmetic emulsion products affect their practical performance. Following manufacture, several months may elapse before the cosmetic is used. Any changes in rheological properties during this storage period may impair their effectiveness. Consequently, to facilitate correct formulation, one must be able to predict rheological changes over long periods of time using a fairly simple and rapid procedure.

Hitherto, estimates of ageing behaviour have been based on accelerated ageing tests at elevated or reduced temperatures (1), stability to high speed centrifugation (1), and more recently on stability to ultracentrifugation at about 40,000 rpm (2–6). These methods are applicable only to relatively unstable, low viscosity, emulsions in which the disperse phase

*Unilever Research Laboratory, Welwyn, Herts.

separates readily in bulk. The rate of separation is assumed to be a measure of stability. Unfortunately the conditions prevailing during accelerated testing are quite different from those to which the cosmetic is normally exposed during storage, so the results are of questionable value. Furthermore, the aforementioned tests provide information only about the final stages of coagulation.

Emulsion coagulation is a three-stage process. Initially, globules flocculate giving rise to aggregates which increase their size with time. Flocculation is a reversible process since the aggregates can be broken down, and the constituent globules redispersed, if adequate shearing forces are applied. Within the aggregates, globules are separated by a thin film of continuous phase. Before globules can coalesce this film must drain away. The rate of drainage depends on the nature of the electrical double layer, viscosity of the continuous phase, temperature, etc. The final stage in coagulation is globule coalescence. This is an irreversible process which leads to a progressive decrease in the interfacial area/unit volume, and eventually to bulk separation of disperse phase. Both flocculation and coalescence influence rheological properties long before there is visible separation of the disperse phase.

This paper describes a method for predicting viscosity changes in emulsions during storage, provided globule coalescence is the only irreversible structural change. It cannot be applied, as yet, to predict changes in emulsions which contain finely divided pigments and/or hydrocolloids which may swell as a consequence of liquid absorption. The method is based upon the fundamental relationship between viscosity and globule size.

Principles of Method for Predicting Viscosity Changes when Emulsions are aged

Most emulsions, apart from very dilute ones, exhibit pseudoplasticity if not plasticity, so that flow properties depend on the applied rate of shear. At high rates of shear, viscosity becomes independent of shear rate and reaches a steady value, but viscosity at low shear rate depends partially on the extent to which the shearing forces have disrupted the globule aggregates.

Globules are rarely of equal size, so size distribution is defined in terms of mean globule size (D_m). Nevertheless, the spread of sizes affects viscosity in addition to the effect exerted by D_m. Very little is known about the influence of the former factor. In general, the relative increase

in viscosity (η_{rel}) rises as D_m decreases. The effect may not be very significant until D_m falls below 5μ when η_{rel} rises exponentially as D_m decreases further (7). Small variations in D_m within the range $0–1\mu$ for emulsions of a given volume concentration disperse phase (φ) cause large changes in η_{rel}.

These observations provide a basis for calculating rheological changes in emulsions when they are aged. If size distribution does not broaden appreciably, the relationship between increasing D_m, due to coagulation, and decreasing relative viscosity at high shear rate (η_∞) should be the reverse of the relationship showing rising η_∞ as D_m decreases (8). One might anticipate some discrepancy between the two relationships at low shear rate because aged emulsions will show a greater degree of flocculation and aggregation than freshly prepared emulsions.

Viscosity at high rates of shear

The influence of D_m on η_∞ is determined by preparing a few emulsions with different values of φ and D_m. Particle size can be varied when using a pressure homogenizer by altering the pressure reading. Alternatively, for a manually operated homogenizer the same effect is obtained by varying the number of passes through the homogenizer. The viscosities of the emulsions are then determined, using a suitable viscometer, at two or more preselected low and high rates of shear.

A plot of η_∞ against D_m for a given φ and constant high rate of shear establishes one of the relationships. Similar plots are made for the other values of φ.

Alternatively, the data can be interpreted in a more useful way. Hydrodynamic interference between globules, which is the principal factor influencing viscosity, is governed by their distance of separation. The mean distance between spherical globules (a_m) can be calculated from

$$a_m = D_m \left(3\sqrt{\frac{\varphi_{max}}{\varphi}} - 1 \right) \qquad \text{(I)}$$

where φ_{max} is the maximum volume of disperse phase which can be incorporated in the emulsion. Most emulsions have a φ_{max} approximating to 74%. A plot of η_∞ against a_m provides a single curve covering all φ values, whereas $\eta_\infty - D_m$ plots are relevant to only one particular value of φ (7).

φ_{max} is reduced if the globules are distorted at high shear rate. In the extreme case, where the globules become prolate ellipsoids, φ_{max} reduces

to 53%. Globule deformation depends on the viscosity ratio of the disperse and continuous phases, the interfacial tension between the two fluid phases, the applied rate of shear, D_m, and the physical properties of the emulsifier layer around the globules. At a shear rate of 1000 sec^{-1} globules smaller than 10μ do not usually distort to any significant extent.

Mean globule size can be calculated in several ways depending on which parameter influences the process studied. For viscosity work D_m represents the mean volume diameter.

$$D_m = \sqrt[3]{\frac{n_1d_1^3 + n_2d_2^3 + n_3d_3^3 - - - - - n_xd_x^3}{n_1 + n_2 + n_3 - - - - - n_x}} \qquad \text{(II)}$$

n_1, n_2, n_3, - - - n_x are the numbers of globules with diameters d_1, d_2, d_3 - - - d_x.

Analysis of published viscosity data concerning well defined suspensions of solid particles in fluid media and emulsions, and our own data for emulsions (9) indicates that

$$\log \eta_\infty = C\left(\frac{1}{a_m}\right) - 0.15 \qquad \text{(III)}$$

where C is a constant which varies with D_m, and can be represented by

$$C = 0.036\,(D_m)^2 \qquad \text{(IV)}$$

If equations (I), (III) and (IV) are combined one obtains the semi-quantitative relationship

$$\log \eta_\infty = \frac{0.036\,D_m}{\sqrt[3]{\frac{\varphi_{max}}{\varphi} - 1}} - 0.15 \qquad \text{(V)}$$

Viscosity at low rate of shear

Apart from the effect exerted by globule coalescence one has now to consider the influence of flocculation on the relative increase in viscosity at low rate of shear (η). Part of the continuous phase is immobilized within the aggregates of globules leading to an apparent increase in φ to $f\varphi$, where f is a "swelling factor." The precise value of f depends not only on the nature of the flocculate, as influenced by the number of globules involved, magnitude of the electrical double layer, ageing time, etc., but also on the rate of shear.

In this respect w/o emulsions are studied more readily than o/w emulsions. The electrical double layer is very diffuse in w/o emulsions.

Globules flocculate very rapidly, so that the influence of aggregation on η shows up from the beginning of the ageing period. The configuration of the absorbed emulsifier molecules at the oil/water interface (steric hindrance) is primarily responsible for stability to globule coalescence (10).

The viscosity exhibited at low shear rate can be viewed as the consequence of hydrodynamic interference between globule aggregates containing immobilized continuous phase.

When estimating globule size by the usual microscopical techniques, the accuracy is limited by the resolving power of the microscope. Apart from globules which are undoubtedly present but cannot be seen, other globules are observed which are so small that their diameter cannot be measured accurately. The globules within this submicroscopic range, i.e. less than 0.5μ, form a negligible proportion of the total number of globules when D_m is greater than 10μ. Alternatively, when D_m is less than 5μ their numbers assume significance. These globules exert a pronounced influence on η, and, as will be shown later, their rapid disappearance during the first three days ageing more than offsets any effect on η due to flocculation. Because of this, $\eta - D_m$ curves for fresh emulsions can be utilized to predict the decrease in η as D_m increases, provided D_m is calculated not as shown in equation (II) but in a somewhat modified way. It is assumed that each emulsion is now a binary mixture of globules. One fraction covers the size range $0–0.5\mu$, whilst the other fraction consists of globules larger than 0.5μ. A mean volume diameter of 0.25μ is assumed for the submicroscopic sized fraction, whilst the mean volume diameter of the larger size fraction is calculated as given in equation (II).

A reasonable assessment of the mean volume diameter for the whole system is given by the mean of the two values taking into account the percentage content of the two fractions.

Rate of globule coalescence

The relationships between globule size and viscosity having been established for both high and low shear rates, one has still to determine the rate at which D_m increases.

If coalescence proceeds independently of the number of globules per unit volume of emulsion then the rate of coalescence (K) depends on the probability of rupture of the liquid film between flocculated globules (11), and on the rupture of hydrogen bonds between molecules in the adsorbed emulsifier layer.

$$N_t = N_o \exp(-Kt) \qquad \text{(VI)}$$

where N_o is the original number of globules per cc and N_t is the number at any ageing time t.

In general,

$$N = \frac{6\varphi \times 10^{12}}{\pi (D_m)^3} \qquad \text{(VII)}$$

so that,

$$\ln D_t = \ln D_o + Kt/3 \qquad \text{(VIII)}$$

Alternatively, D_t can be calculated (12) from

$$(D_t)^3 = (D_o)^3 + \frac{8\,kT\,\varphi\,t}{\pi\,\eta_o} \exp\,(^{-E}/RT) \qquad \text{(IX)}$$

where k is the Boltzmann constant, T is the absolute temperature, E is the activation energy required for coalescence, and η_o is the viscosity of the continuous phase.

When emulsions contain globules smaller than 0.5μ diameter K in equation (VIII) and E in equation (IX) do not remain constant throughout the whole ageing period (13). For the first two or three days K has a relatively high value, and E has a low value, due to a correspondingly faster rate of coalescence. When the submicroscopic size globules have disappeared coalescence proceeds according to equations (VIII) and (IX). The processes which effect stability, e.g. film drainage, adsorption at the oil-water interface, are not governed by the usual laws when a globule has a high radius of curvature.

Ageing tests should be continued, therefore, until such time that the linearity of the $\ln D_t$ – t or $(D_t)^3$ – t plots for the slower phase of coalescence are well established. This should not take more than about a week at the utmost. Values for K or E can then be calculated. These data taken in conjunction with the $\eta_\infty - D_m$ or $\eta - D_m$ graphs, or equations (V) or (VI), enable one to calculate viscosity changes for extensive ageing periods.

Results

Water-in-liquid paraffin emulsions stabilized with sorbitan mono-oleate, and liquid paraffin-in-water emulsions stabilized with sorbitan mono-laurate, were studied over a wide range of φ values. The initial value of D_m was varied by one to six passes through a hand operated valve homogenizer. All viscosities were measured with a Haake "Rotovisko" viscometer

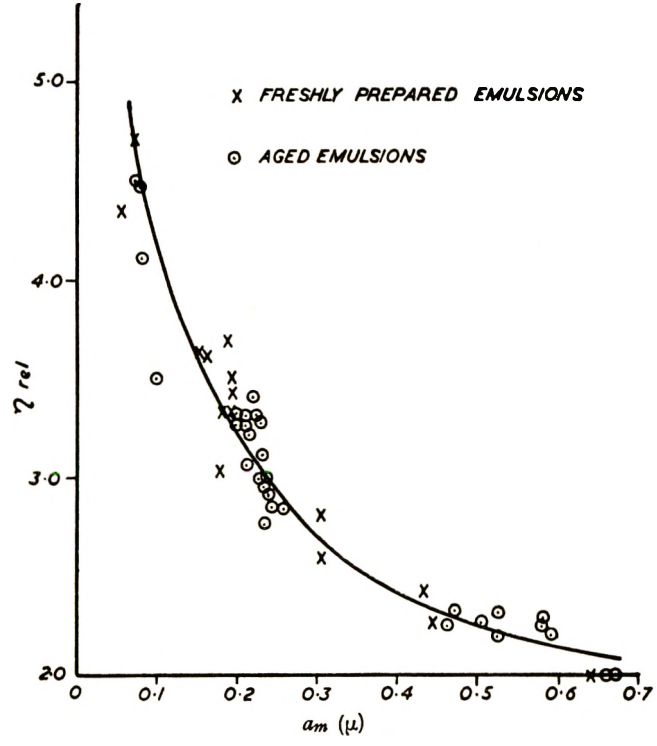

Figure 1

The influence of a_m on η_{rel} for aged water-in-liquid paraffin emulsions

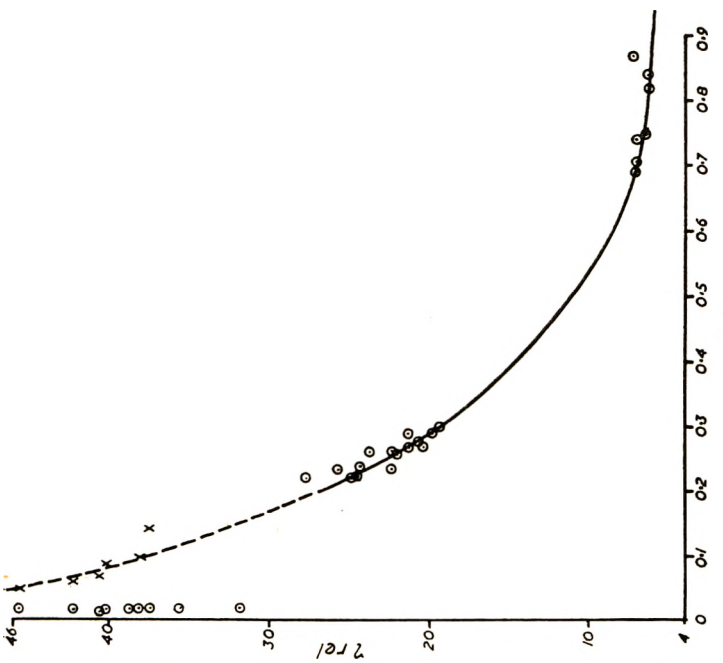

Figure 2

The influence of a_m on η_{rel} for aged liquid paraffin-in-water emulsions

Using equations (VIII) and (IX), the values of C and E for slow phase coalescence were calculated.

	E (k cal/mol)	C ($sec^{-1} \times 10^{-8}$)
O/w emulsions	6 – 7	17.7
W/o emulsions	6 – 7	31.9

Figs. 1 and *2* show the $\eta_\infty - a_m$ relationships for w/o and o/w emulsions respectively. In both cases the data for freshly prepared and aged emulsions fall on the same curve. The curve for the o/w emulsions deviates from the exponential form at high values of φ due to the globules being somewhat distorted when closely packed. Taking these curves in conjunction with the quoted values for E and C it was possible to construct theoretical curves for the change in η_∞ with ageing time. *Figs. 3* and *4* indicate that the theoretical predictions and the actual experimental data agree very satisfactorily (8).

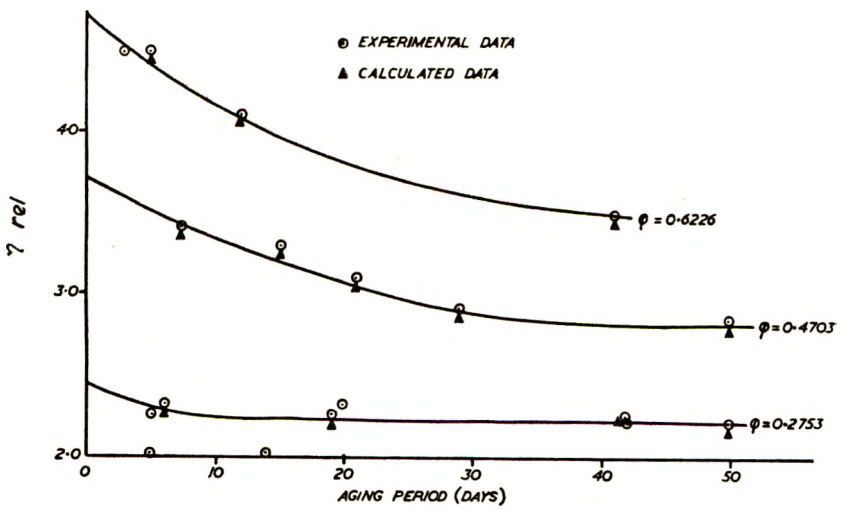

Figure 3

Water-in-liquid paraffin emulsions—Comparison of experimental and theoretical changes in η_{rel} on aging

Studies at low shear rate have been confined to w/o emulsions in which the globules flocculated very rapidly. When D_m was calculated by equation (II), which reduces to insignificance any effect due to very small

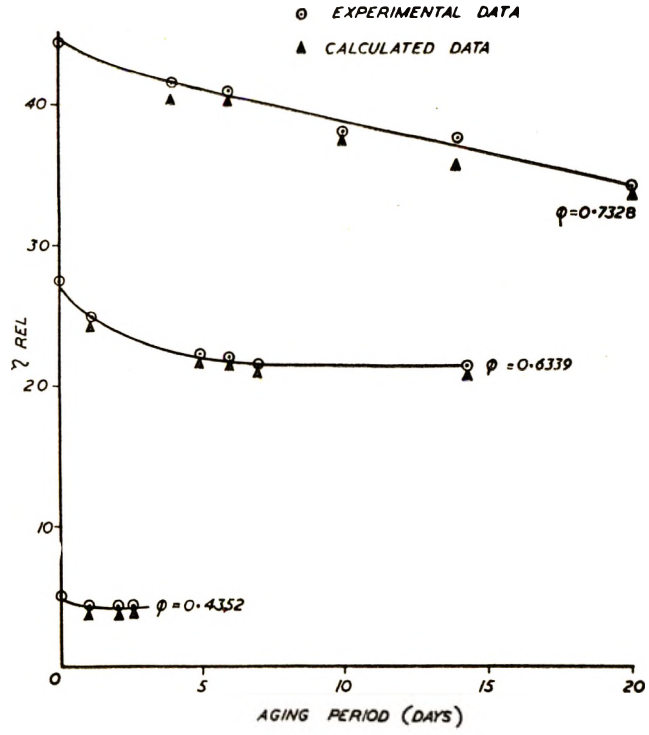

Figure 4

Liquid paraffin-in-water emulsions: comp. of experimental and theoretical changes in η_{rel} on aging

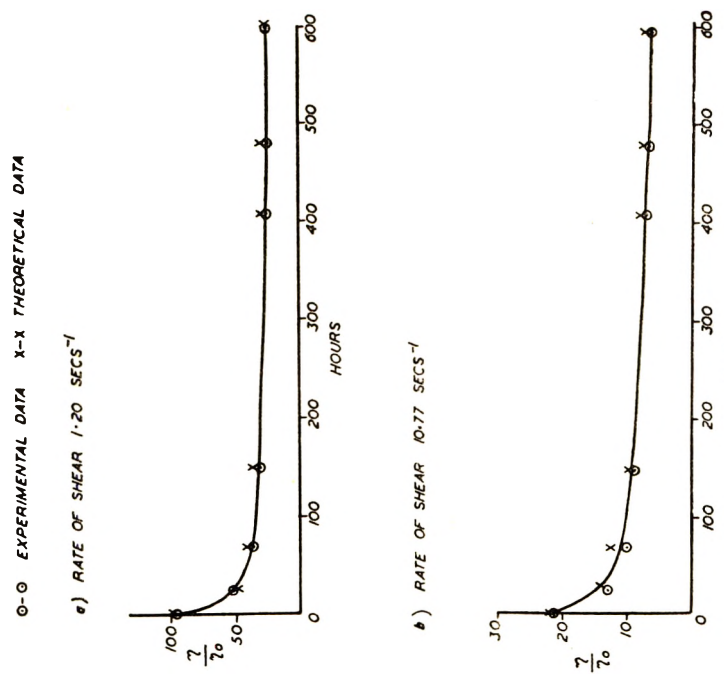

Figure 5

Comparison of experimental and calculated changes in η/η_0 on aging

globules, it was found that $\eta - D_m$ plots for fresh and aged emulsions did not coincide. For any D_m selected, the fresh emulsion always had a higher η than the emulsion which reached this same D_m after a period of ageing. Similarly, when emulsions reached a selected D_m after different short ageing times the shorter time the emulsion had aged the higher its value of η. These divergencies disappeared after longer ageing periods. Using the modified procedure for calculating D_m good correlation was achieved at two different low rates of shear – 1.20 sec^{-1}, and 10.77 sec^{-1} between theoretical predictions and experimental data (*Fig. 5*).

The influence of flocculation on the rheological properties of an aged concentrated w/o emulsion

A w/o emulsion ($\varphi = 47\%$) was aged for several days. Each day a sample was withdrawn, stirred for five min at 215.5 sec^{-1} at 21°C, and the rate of viscosity recovery at 1.33 sec^{-1} was then studied.

An appreciable breakdown of structure occurred at the higher shear rate. The freshly prepared emulsion gave a viscosity of 10.5 poise after shearing for 5 min at 215.5 sec^{-1}. Subsequently the viscosity rose to 139 poise at 1.33 sec^{-1} (*Fig. 6*). The latter value was reached in about 30 sec with most of the recovery occurring with 10 sec of switching over to the low shear rate. Emulsions aged for 24–189 hr gave viscosities similar to that of the fresh emulsion after shearing for 5 min at 215.5 sec^{-1}. Following structural recovery at 1.33 sec^{-1} large differences were apparent between fresh and aged emulsions. The longer the emulsion had been aged, the lower the final steady-state viscosity. The major drop in steady-state viscosity took place during the first 24–44 hr of ageing. This corresponds to the time taken by globules less than 0.5μ diameter to disappear by coalescing with larger globules or between themselves.

From the data given in *Fig. 6* one can calculate the apparent increase in φ due to flocculation. Mooney (14) interpreted thixotropic recovery from similar data using an empirical $\eta_\infty - \varphi$ equation

$$\eta_\infty = \frac{\sqrt{1 + 0.5\,\varphi}}{1 - \varphi} \exp\left(\frac{1.25\,\varphi}{1 - \varphi}\right) \qquad \text{(X)}$$

It will be noted that equation 10 does not allow for the influence of globule size on η_∞. A more representative curve relating η_∞ to φ can be derived by equation V. The apparent φ for any sample is obtained by referring the measured η at 1.33 sec^{-1} to this curve and determining the

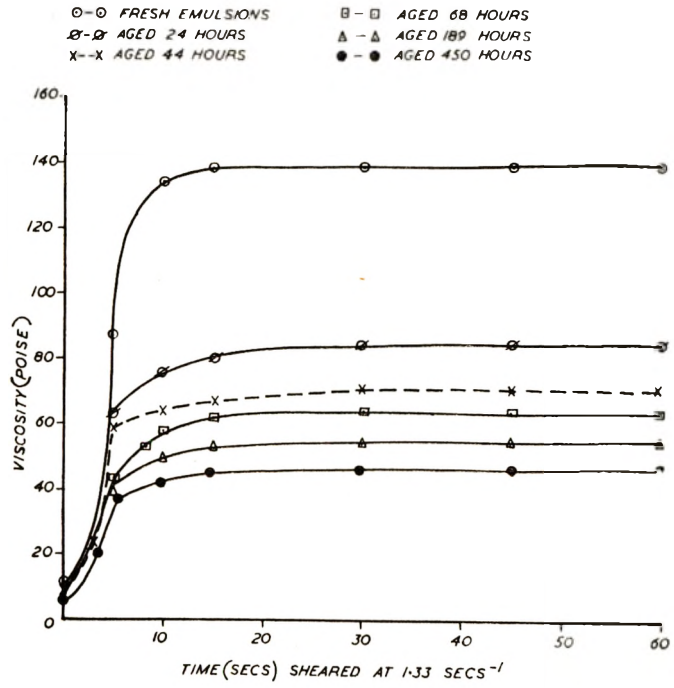

Figure 6

Structure recovery at 1.33 sec^{-1} after shearing for 5 min at 215.46 sec^{-1}

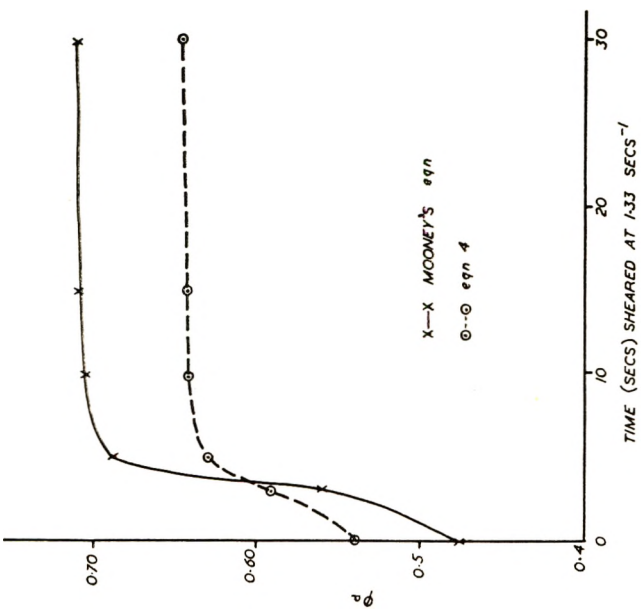

Figure 7

Apparent volume fraction disperse phase at different intervals of shearing at 1.33 sec^{-1} after shearing for 5 min at 215.46 sec^{-1}

corresponding φ. Accounting for the influence of D_m in this way results in an apparent increase in φ at the steady state which is less than that suggested by equation X (*Fig. 7*).

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DISCUSSION

MR. M. J. THORNTON: The paper implies that the rheological properties are those of a Bingham plastic at higher shear rates, i.e. the viscosity is independent of rate of shear above a certain value. Have you tried to fit the curves obtained to any published rheological equation?

THE LECTURER: There are two types of rheological equation that one can apply, and I am not quite sure which one you are referring to. You have first of all the stress-rate of shear type of equation which one can try to use. The other type relates viscosity to the volume concentration of disperse phase and other components of the emulsion. All these equations suffer the disadvantage that the authors have applied them to their own data but have very rarely tried to apply them to any other data. As soon as you try to do this you run into trouble.

We have not looked at the stress-rate of shear relationship because we were not studying the problem as a basic rheological one.

We have tried to relate viscosity to volume concentration, etc., and in a review (15) we have discussed this particular question in great detail. When developing equations of this type, the great tendency has been to try and devise an equation which is an extension of the original equation of Einstein, and people tend to forget the limitations imposed by Einstein on the applicability of his equation. They have tried to introduce factors, apart from the straightforward relationships between the viscosity and the volume concentration of disperse phase, which in essence are powers of the volume concentration. There is a wide range of such equations which has

(15) *J. Pharm. Pharmacol.* **16** 1 (1964).

been published in the literature over many years. You will find that when you get on to the powers of the volume concentration the multiples involved vary from paper to paper. This, I think, is essentially due to the fact that people have ignored the effect of particle size. It is only in the past few years, in work such as that of Saunders of the Dow Chemical Company in the U.S.A., that the influence of particle size on viscosity has been clearly demonstrated. He worked with extremely dilute systems, but nevertheless showed that if you have very small particles, about 1 μ down to 1,000 Å units, then even in the range where Einstein's original equation is supposed to apply you are getting a particle size effect, and this must be taken into account. The only comfort I can give so far is the fact that equation (V), which we developed by analysing our own data and that of other people, does seem to apply to practically all viscosity data that we can find where the particle size is specified fairly accurately.

In addition, the question of particle size distribution has also to be considered. You can obtain the same mean particle size with different size distributions, and you can run into trouble because of this. What we have tried to do is to get a rough assessment of the effect due to the sub-microscopic size particles, because in any way that you work out your mean size, apart from using the simple arithmetical mean, you get involved in powers of the particle size. When you are dealing with sub-microscopic size droplets, once you start taking powers of their diameters they reduce to insignificance. For the moment the best that we can do is to get a rough assessment of the visible sub-microscopic size particles by assuming a mean diameter of 0.25 μ, work out the mean size for the larger droplets in the normal way, and then take an arithmetical mean of the two values. By doing this we find that we can allow for the influence of these sub-microscopic size particles to a certain extent. This particle size effect has, in fact, been virtually ignored over the years, with the result that the interpretation applied to published literature is completely incorrect, because many of the effects which are supposedly present are due, in fact, to variation in particle size and nothing else.

MR. M. J. THORNTON: The postulated instability of globules smaller than about 0.5 μ is presumably the main reason for viscosity changes on ageing. What theoretical background is there for this idea and what influence has the amount and type of emulsifying agent on the stability of emulsions?

THE LECTURER: These droplets are responsible for viscosity changes only in the very initial stages of ageing; as I mentioned, they disappear fairly quickly, and you get quite sharp viscosity changes during this period. Subsequently the main factor is the coagulation of the larger size droplets.

The whole idea has been discussed in a recently published paper (13). A viscous type emulsifying agent will increase the viscosity of the continuous phase and therefore decrease the rate at which the globules will come together. The actual coalescence, as distinct from flocculation which is only the first stage of coagulation, depends very much on whether your emulsifying agent forms a layer which is one or more molecule thick round the droplets. For instance, for a material such as protein it is very well established that you can get a layer which is many molecules thick around the droplets. We have been able to alter the rate of coalescence of droplets in a dilute emulsion, such as an ice cream mix, containing 10 per cent fat-in-water stabilized by milk protein, by increasing the amount of the milk protein, because this layer of protein around the droplets then becomes progressively thicker.

Take the example of w/o emulsions stabilized by the nonionic emulsifying agents *Span 80* or *Span 85*. It is fairly certain that these emulsifiers, irrespective of the concentrations used, form a layer which is only one molecule thick around the fat droplets. Therefore you cannot alter the rate of coalescence by adjusting the amount of emulsifier. You may alter other processes such as flocculation, but certainly not the rate of coalescence once the droplets have flocculated.

MR. M. J. THORNTON: Is D_m a volume or weight mean particle size? What effect did six passes through a hand homogenizer have on this figure and how was it determined? It can presumably refer to more than one size distribution depending on the spread of globule sizes present. This does not seem to have been taken into account in any of the theoretical equations advanced.

THE LECTURER: This depends very much on the volume concentration of dispersed phase. In very highly concentrated systems you will find a progressive decrease in particle size and also a narrowing of the size distribution with repeated homogenization. If you apply this same technique to a very dilute system you get such efficient dispersion after the first passage through a manually operated homogenizer that the subsequent passes will make very little difference. The effect depends very much on the volume concentration of the dispersed phase.

MR. R. L. STEPHENS: Do aged emulsions return to their original viscosity if they are rehomogenized?

THE LECTURER: You can not re-emulsify these emulsions once they have broken down. I do not think this is due to hydrolysis of the emulsifying agents; in this particular type of system you seem to get some sort of solid precipitate formed at the interface following adsorption of emulsifier. Once this has been displaced from the interface you cannot put it back again. This also applies with protein-stabilized emulsions. You get denaturation following adsorption at the interface; therefore the protein has changed its condition and cannot be used again. You can only re-emulsify by introducing some more emulsifying agent. I would never recommend making an emulsion in this way, because one has to be very careful about the initial stages of dispersion in preparing an emulsion. You must add only a few droplets at a time of the material which is going to be dispersed, and make sure that this disperses really completely before adding any more rather than bulk introduction. A good emulsion is never obtained by adding the liquid to be dispersed in bulk.

MR. R. L. STEPHENS: Is there in fact a "no-man's-land" of instability of emulsions between gross particle sizes of the order of 0.5 μ and colloidal solutions of a micellar nature?

THE LECTURER: A lot of change can be going on in the system without any visible change. This is the point I am trying to make. Particularly when submicroscopic or very small particles are present, the actual size distribution, and the average size, may appear to undergo very little change – whereas in actual fact there has been a substantial decrease in the number of droplets. You can, for instance, start off with a system containing perhaps a million or more droplets per cc of emulsion. Although you get no apparently visible change in the emulsion, that number might have dropped by one or two orders of magnitude. The only instance I know where systems are fairly stable – and references in published literature

have been based upon this – are latex emulsions where the stabilizer is of a rather different type and 'limited coalescence' is reported. There is a small change during the first 24–48 hr, and after that very little further change. I suspect that this might also be due to the fact that the rate of disappearance of very small particles has not been studied in detail nor appreciated.

MR. H. E. GARRETT: Mr. Stephens's second question was settled by G. S. Hartley in the late 1930's. In the micelles containing oils in solution you have a low vapour pressure of a solute. In an emulsion the vapour pressure of the solute, the larger particle sizes, is equal to the normal vapour pressure, but as the particle size of the emulsion decreases one gets an increased vapour pressure or solution pressure, as the case may be. Before you get down to the micelle region the vapour pressure becomes quite considerable, so that there is a region of sizes which cannot be attained with any degree of stability at all.

THE LECTURER: I would like to add that certain work has been done in the U.S.A. on nonionic emulsifying agents which indicates that even in the micellar state they are not stable; in that case you get progressive breakdown of the micelles.

MR. C. PARRY: You quote φ_{max} being approx. 74%. I would like to point out that this applies to rigid spheres of equal diameter. As you say it does have some effect. And later on you point out that you get deviations at high φ as in *Figs. 1* and *2*. Has there been any attempt by any workers to apply correction factors to overcome this effect?

THE LECTURER: Nobody has studied this in any great detail. As you say, it does really apply to rigid spheres. Nevertheless, in all the systems that we have studied it was also applicable. I know that there is a lot of talk in the literature that one can make emulsions of 90% or more disperse phase, but personally I have never believed this. I have always suspected that these people have never looked at the structure of their emulsions once they have made them. We have certainly found that with this type of system – and we have studied this very carefully – we can in fact, when doing it manually, introduce 85 to 90% of disperse phase; but once you get above about 75% to 76% you are ending up with an emulsion made up of many phases. It is not a simple emulsion.

Very little work has been done on this to establish whether droplets are deformable so they can in fact become ellipsoids. It is a very complex problem, and so far, apart from analyses of the effect on viscosity of using pure ellipsoidal systems, the actual effect of deforming spheres into ellipsoids has not been studied.

MR. J. G. PITT: I have been trying to relate these equations in a practical way to predicting the changes in viscosity, without the necessity of going through particle size counting. It seems to me that if this log D-t graph does in fact flatten out, then equations (VIII) and (V) could be combined and give a very much simpler form in which the log of viscosity plotted against time would eventually flatten out and give a linear relationship which could be used to predict future viscosities, assuming this semiquantitative equation which you have here. Could you say if this is a feasible procedure?

THE LECTURER: One of the snags you are up against is the effect of the rate of shear. We have only studied the effects at one or two rates of shear, but the rate of viscosity recovery is very much lower as you go down to rates of shear of about

0.1–0.2 reciprocal sec. In actual fact one has to introduce a factor which includes the effect due to rate of shear on this process. That is why I personally, at the moment, would not be inclined to make too much use of the equations quoted here, but in actual fact, and in this way one can allow for any deformation of the particles, I would prefer to work out a viscosity-particle size relationship independently for each system one is studying. There is not enough information really to apply these equations with any degree of accuracy to one's predictions.

MR. W. R. WEBB: Would you please, perhaps, enlarge on the method of particle size analysis used in this work; perhaps you can comment on methods that can be used on particle size analysis of emulsions; and perhaps, too, could you comment on the use of the Coulter counter for this work?

THE LECTURER: This is a very vexed problem. The method we used here was just a simple microscopic technique with very large magnifications, grouping the droplets into small increments of size of about 0.5 μ, a.s.o., calculating the number in each particular increment, and then, because volume effects were involved in viscosity, working out the average size as given in equation (II). We are now inclined to think that possibly we can study the smaller size particles more accurately by getting onto light scattering techniques. This has been used in the past to a certain extent with solid polymer beads, but to the best of my knowledge very little work of this type has been done on deformable droplets which are dispersed in another liquid. The only other method I know of which has been used to any great extent is one developed by Dr. Goulden (National Institute for Research in Dairying), in which he used a Hilger absorptiometer in slightly modified form. In essence he initially developed a technique to measure the volume disperse phase of a system assuming standard particle size. He has now gone the other way round, taking a standard volume fraction, and tried to find the effect of turbidity on particle size. He found a relationship between turbidity, a fairly simple measurement, and particle size down to about 0.5 μ. The relationship was a linear one, and therefore by extrapolating the relationship backwards, he assumed that you could go down to still smaller particle sizes. He now claims that he can go down to about 0.2 μ, and that he has cross-checked this with measurements with the electron microscope. Unfortunately this technique gives you an average surface area diameter and nothing else. It gives no indication of the spread of particle sizes. As this has a fairly large effect on viscosity, even if you measured your average size this way, you would have to resort to some other means to get an assessment of average distribution of particle sizes.

I have no personal experience of the Coulter counter instrument, but I understand both from the manufacturers and from people who have used this, that once you get to 1 μ or below it is ineffective; you cannot measure very small sizes accurately.

MR. W. R. WEBB: In the literature, people did fantastic numbers of counts. I wonder if you could indicate the number of counts that you carry out.

THE LECTURER: We normally count about 500–600 globules, and in this way we find that we get very satisfactory reproducibility on duplicate samples. It is unnecessary to go into thousands or tens of thousands as some people have done.

J. Soc. Cosmetic Chemists **16** 607-615 (1965)

Application of Attenuated Total Reflectance IR spectroscopy to toilet articles and household products, 1.—Qualitative analysis

N. A. PUTTNAM, S. LEE and B. H. BAXTER*

Synopsis—The application of IR spectroscopy to the identification of components in toilet articles and household products using a special reflection technique, i.e. Attenuated Total Reflectance, is described. This technique, which is essentially independent of sample thickness, permits spectra to be obtained from bulk samples which are equivalent to those obtained by transmission through thin films. Such a procedure overcomes the experimental difficulties encountered when attempting to study these types of products by transmission spectroscopy.

Examples are quoted of the application of ATR, without any prior sample preparation, to soap-detergent combination bars, toothpastes, washing-up products, all-purpose cleaners, shampoos and bubble baths.

Introduction

The recent advent of a special reflection technique, namely Attenuated Total Reflectance (ATR), has greatly facilitated the application of infrared spectroscopy to toilet articles and household products.

ATR was developed by Fahrenfort (1) for the determination of optical constants and as a means of obtaining intense spectra from samples which were difficult or unamenable to study by normal transmission techniques. Simultaneously Harrick (2) developed a multireflection technique to obtain spectra from surface layers. In this case the surface was sampled many times and hence weak absorptions were magnified. In ATR the radiation incident on an interface (at angles of incidence greater than the critical angle) between the sample and an analysing crystal of higher refractive

*Research and Development Dept., Colgate-Palmolive Ltd., Manchester, 5.

index will be totally reflected at those wavelengths where the sample shows no absorption. However, at wavelengths where the sample absorbs, part of the incident radiation will be absorbed causing an attentuation of the reflected radiation. Such an effect produces a spectrum which strongly resembles the transmission spectra, although the shape of the bands will be different (3).

Since the technique depends upon attenuation of the reflected energy at the interface it is essentially independent of sample thickness. Hence, by this technique spectra can be obtained from bulk samples which are equivalent to those obtained by transmission through thin films. Such a technique eliminates (a) the need to obtain reproducible thin films, (b) the difficulties encountered in filling short path-length cells with viscous liquids, and (c) the troublesome interference patterns found with such cells. Also, for aqueous solutions there is no need to compensate for the very strong solvent absorptions.

Experimental

The ATR spectra were recorded on *Unicam SP100* and *SP200* IR spectrometers using a TR-3 ATR attachment, manufactured by *Research and Industrial Instruments Co.* This attachment provided for the examination of solid or liquid samples at angles of incidence within the range 26 to 63°. A KRS-5 prism was used as the analysing crystal for all except highly alkaline samples, where an Irtran II prism was employed. Since the transmission of both prisms was only 60 to 70% it was necessary to attenuate the reference beam. This attenuation was carried out by placing a beam attenuator in the reference beam and adjusting to an absorbance value of 0.07 to 0.1 at a wavelength where the sample showed no absorption.

For solid products, the sample was pressed against the back face of the prism with a clamping plate. For this type of sample the angle of incidence was between 38 and 33° and the spectrum recorded over the wavelength range 600 to 5000 cm^{-1}.

If the sample was a cream, a thick layer was smeared onto the back face of the prism and the spectrum recorded as described above.

For liquid products a backing plate, with a Teflon seal, was fitted to the prism mount to form a sealed cell, approximately 2 mm thick, on the back face of the prism. The sample was then introduced into this cell through the filler-ports with a syringe, and the spectrum recorded at an angle of incidence between 33 and 40°.

After each spectrum had been recorded the prism was removed from its mount and cleaned by lapping on a polished pad with *iso*propanol for 60 sec.

Results and Discussion

As has been found previously (4,5) the intensity of the bands increased as the angle of incidence decreased. It was further found, particularly for solid samples, that the resolution varied with the angle of incidence. In the case of sodium salts of fatty acids decreasing the angle of incidence improved the resolution in the region of 2800 cm^{-1} but caused a deterioration in the region of 1450 cm^{-1}. For each type of sample it was therefore necessary to carry out a preliminary study to determine the optimum angle of incidence.

Although the transmission of the Irtran II prism was less than that of the KRS-5 prism, in the wavelength range 900 to 650 cm^{-1}, the former was used for highly alkaline samples since they caused the formation of a bright yellow film on the KRS-5 prism. Aqueous solutions produced a white "bloom" on the KRS-5 prism. Although no absorptions, due to the bloom, could be detected it appeared to absorb some of the solute and lead to erroneous results. Polishing with *iso*propanol on a lap for a few seconds was sufficient to clean the prism.

Fig. 1 shows the ATR spectra of a sample of toilet soap, which contained ca. 11% moisture, together with those of two typical detergents used in soap-detergent combinations bars (combars), namely the sodium isethionate ester of coconut oil acid, and talloyl methyl tauride. Also shown are the ATR spectra of two combination bars.

In the case of combar A (*Fig. 1c*) the absorptions at 1550 and 1405 cm^{-1}, due to an ionised carboxylic grouping, together with the absorption at 930 cm^{-1} indicated that the major component was soap. The absence of absorptions within the wavelength range 1720 to 1740 cm^{-1} showed that ester-containing components were absent. The absorption at 1640 cm^{-1} was due to a tertiary amide grouping, since there was no evidence of the Amide II absorption at ca. 1515 cm^{-1}. The spectrum also showed strong absorptions at 1185 and 1060 cm^{-1} which could be ascribed to the asymmetric and symmetrical SO_2 stretching vibrations of an ionic sulphonate. Comparison with spectrum 1(*b*) showed that the detergent in this combination bar was a talloyl methyl tauride.

The ATR spectrum of combar B (*Fig. 1d*) showed absorptions at 1550, 1405 and 930 cm^{-1} which indicated the presence of soap; the soap content

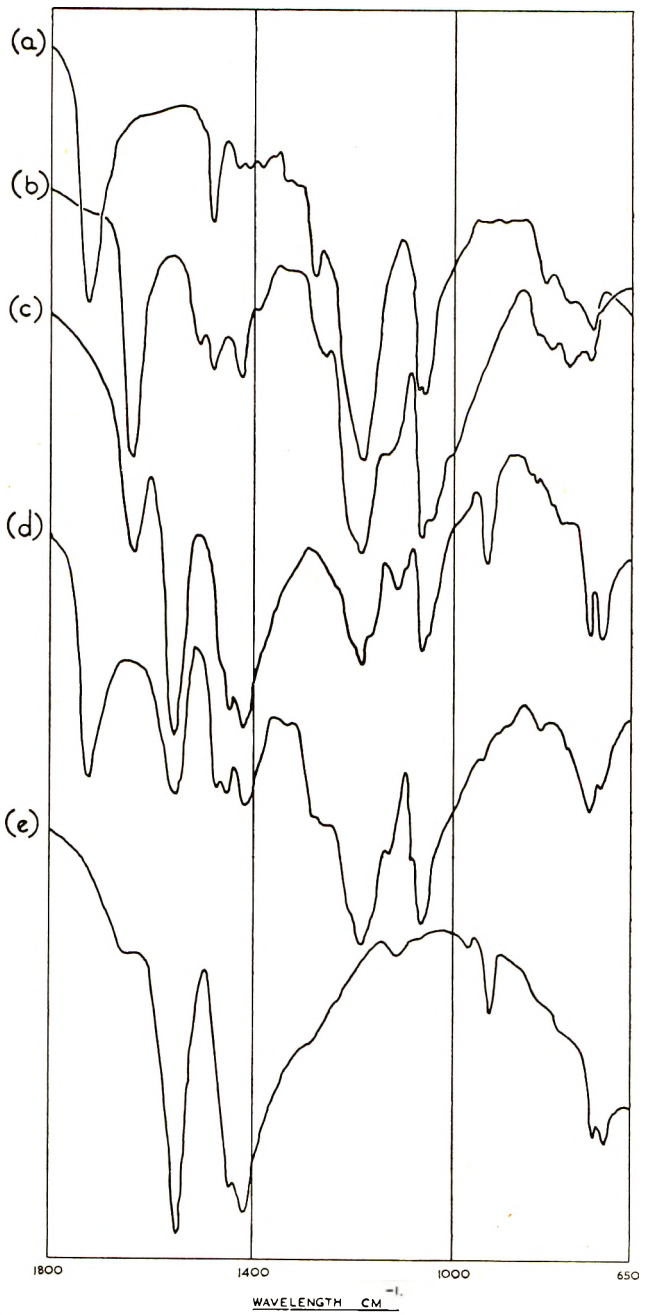

Figure 1

ATR spectra of

(a) sodium isethionate ester of coconut oil acid R.COO CH_2 CH_2 SO_3 Na
(b) talloyl methyl tauride R.CO N (Me) CH_2 CH (OH.) SO_3 Na
(c) combar A
(d) combar B
(e) toilet soap, containing ca. 11% moisture.

was less than that in combar A. The strong absorptions at 1185 and 1060 cm^{-1} indicated the presence of an ionic sulphonate, which was not attached to an aromatic ring since there were no absorptions at 1610 and 840 cm^{-1}. The absorptions at 1730 cm^{-1} showed the presence of an ester grouping and comparison with spectrum *1a* showed that the detergent in combar B was the sodium isethionate ester of a fatty acid.

The ATR spectra of three toothpastes are shown in *Fig. 2.* The absorptions at 1120, 1052, 1002 and 940 cm^{-1} for *A* and *B* were due to

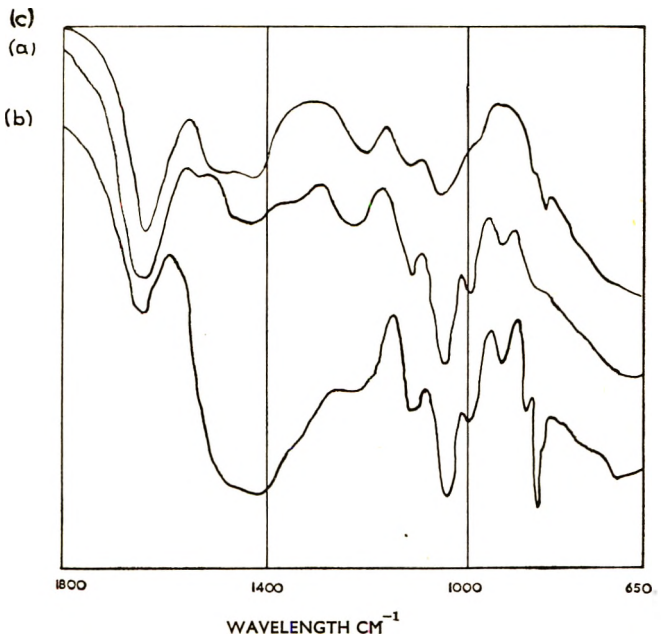

Figure 2. ATR spectra of toothpastes.

glycerol while that at 1640 cm^{-1} was due to water. The very broad strong absorption at 1410 cm^{-1} and the doublet at 860 and 885 cm^{-1} in the ATR spectrum of toothpaste *B* (*Fig. 2b*) showed that it contained a large amount of a carbonate which was not present in the other toothpaste. The spectrum of *C* showed a low concentration of carbonate together with sorbitol shown by the broad weak absorptions at 980 to 1120 cm^{-1}.

Fig. 3 records the ATR spectra of three liquid washing-up products. The absorptions at 1090, 1050 and 890 cm^{-1} in the ATR spectrum of *A* (*Fig. 3a*) showed that it contained ethanol, while the absorptions at 1180,

1130 and 1020 cm^{-1} indicated that a dodecylbenzene sulphonate was present. The absorptions at 1200 cm^{-1}, due to the asymmetrical SO_2 stretching vibration, and 930 cm^{-1} showed that an ionic sulphate was also present. The other characteristic absorption shown by such sulphates, which occurs at ca. 1050 cm^{-1}, would be hidden by the ethanol absorption at 1050 cm^{-1}. It was concluded therefore that the active ingredient in *A* was a mixture of a sulphonate and a sulphate. The shoulder at 1250 cm^{-1} showed that an aromatic ether grouping was present, which may be associated with the ionic sulphate. The alternative would be that this grouping was associated with an ethoxylated alkylphenol present as a nonionic.

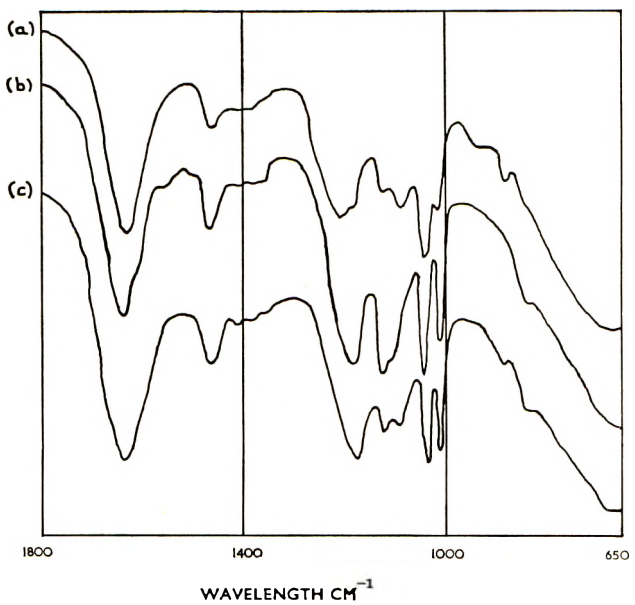

Figure 3. ATR spectra of washing-up liquids.

Since there was no absorption at 890 cm^{-1} in the ATR spectrum of *B* (*Fig. 3b*) it did not contain ethanol. The absorptions at 1180, 1130, 1040, 1015 and 840 cm^{-1} showed that this product contained a dodecylbenzene sulphonate. As the intensity of the absorption at 1015 cm^{-1} was less than that of the absorption at 1040 cm^{-1}, by comparison with reference sample, there were no toluene or xylene sulphonates present. The absorption at 1110 cm^{-1}, due to aliphatic ether groupings, and those at 1630 and 1550 cm^{-1}, due to an amide group, suggested that this product contained an ethoxylated fatty amide as a nonionic.

Since there were weak absorptions at 1050 and 890 cm^{-1} in the ATR spectrum of *C* (*Fig. 3c*) it contained a relatively small amount of ethanol. The absorptions at 1180, 1130, 1040, 1015 and 840 cm^{-1} were due to a dodecylbenzene sulphonate. There was, however, an absorption at 1090 cm^{-1} and the intensity of the absorption at 1015 cm^{-1} was almost equal to that of the absorption at 1040 cm^{-1}. By comparison with reference spectra these results showed that *C* contained dodecylbenzene and xylene sulphonate. The absence of absorptions at ca. 1630 and 1550 cm^{-1} showed that the nonionic was not derived from a fatty amide.

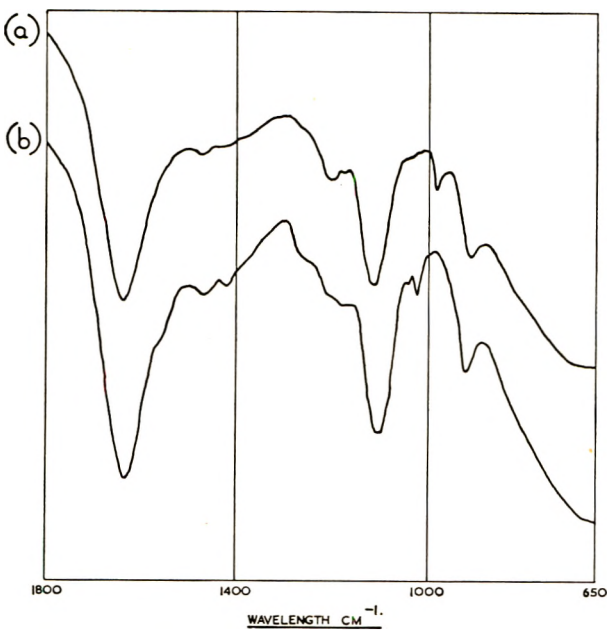

Figure 4. ATR spectra of liquid all-purpose household cleaners.

The ATR spectra recorded in *Fig. 4* were of two liquid all-purpose cleaners. That both products contained a pyrophosphate was shown by the absorptions at 1210, 1110 and 925 cm^{-1}. Since the intensity of the absorption at 1180 cm^{-1} was low in the case of *A* (*Fig. 4a*) it only contained ca. 1% sulphonate. However in *B* (*Fig. 4b*) this absorption was more intense showing that the sulphonate content was greater. Further, since there were absorptions at 1020 and 1040 cm^{-1} at least part of this sulphonate occurred as the xylene sulphonate. An absorption at 1560 cm^{-1} in *B* indicated that it also contained soap.

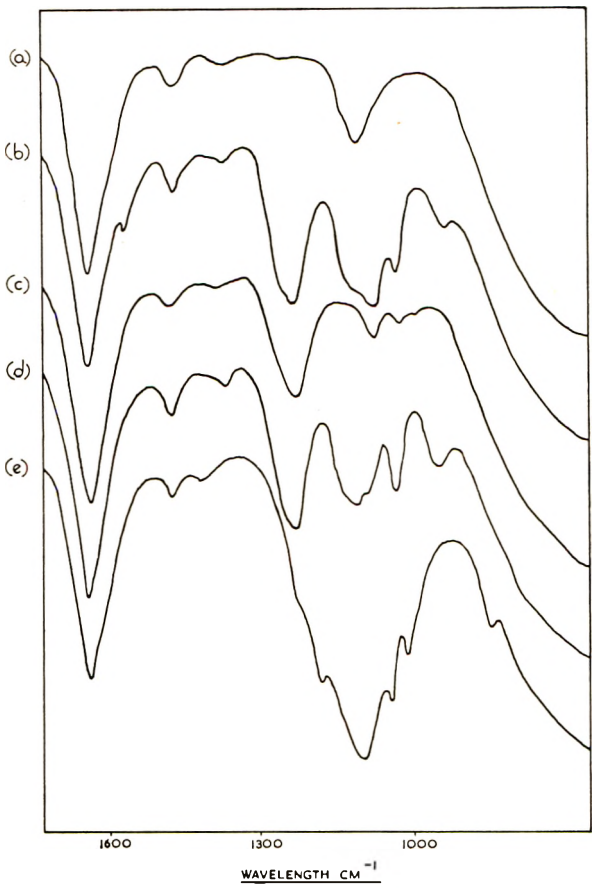

Figure 5. ATR spectra of shampoos and bubble baths.

In *Fig. 5* is recorded the ATR spectra of three shampoos (*Figs. 5a, 5c* and *5d*) and two bubble baths (*Figs. 5b* and *5e*). As no absorptions were detected within the wavelength range 1150 to 1250 cm^{-1}, for *A*, it did not contain a sulphate or sulphonate. The absorption at 1110 cm^{-1}, due to an aliphatic ether linkage, showed that the major component of this product was an ethoxylated fatty alcohol. The spectrum of *B* (*Fig. 5c*) showed an absorption at 1220 cm^{-1}, due to a sulphate, but there was no evidence of an ether absorption at 1110 cm^{-1}. Hence it was concluded that the active ingredient in this product was a sulphated fatty alcohol. In the case of *C* (*Fig. 5d*) the absorptions at 1220 and 1110 cm^{-1} showed that it contained a sulphated fatty alcohol ethoxylate as the active ingredient.

Since there was an absorption at 1560 cm^{-1} in the spectrum of bubble bath *A* (*Fig. 5b*) it contained soap together with a sulphated fatty alcohol ethoxylate; the presence of the latter was indicated by the absorptions at 1220 and 1110 cm^{-1}. In the case of bubble bath *B* (*Fig. 5e*), the absorptions at 840, 1010 and 1040 cm^{-1}, associated with the sulphonate absorption at 1180 cm^{-1}, showed that it contained an alkylbenzene sulphonate. The very broad absorption centred at 1100 cm^{-1} was due to the presence of inorganic sulphate.

In all cases the thickness of the sample on the back of the prism was at least 1 mm, since it has been shown (6) that for samples less than 10μ thick, particularly solid samples, ATR spectra are dependent upon sample thickness.

The examples quoted above show the type of information that can be obtained very simply, without any prior sample preparation, by the ATR technique. This technique is, of course, rather insensitive for minor components, the actual sensitivity being dependent upon the intensity of the infrared absorption bands, since ATR spectra are comparable with those obtained by transmission through a 5 to 10μ thickness of sample.

In theory there is a unique ATR spectrum for each angle of incidence. With a prism as the analysing crystal the beam, within the prism, is not collimated and hence the spectra recorded were for a range of angles. Since the spectra were recorded close to the critical angle, to obtain the most intense spectra, they may have contained contributions from transmission and reflection spectra. Fahrenfort suggested (1) that this could be overcome by using a hemi-cylinder with an external focus, which produces a collimated beam, as the analysing crystal. In practice, however, this is not the case since the performance of the hemi-cylinder is not in accordance with theory. This is due to the shape of the hemi-cylinder being altered by stress, when the sample is pressed against it, and by polishing to remove dents and bruises caused by the sample.

The quantitative aspects of the application of ATR to toilet articles and household products will be dealt with in a future publication.

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The influence of lanolin derivatives on dispersed systems, 1. The dispersion of pigments in nonaqueous liquids

L. I. CONRAD, H. F. MASO, and SHIRLEY A. DeRAGON*

Presented at the Symposium on "Emulsions", organized by the Society of Cosmetic Chemists of Great Britain at Harrogate, Yorks, on 1st April 1965.

Synopsis—The dispersing activity of several lanolin derivatives is studied by means of modified wet and flow point procedures which are described in detail. Sedimentation tests and microscopic examination are used as supplementary aids. These procedures reveal significant pigment wetting and deflocculating activity for lanolin derivatives when used as additives. The wet and flow point measurements provide quantitative data which can be used to determine efficient additive/pigment ratios for each system studied.

Because of the specific action of the wetting additives no single lanolin derivative can be recommended for all pigment/vehicle systems, but an ideal dispersing aid might utilize a combination of these surface active materials.

Introduction

The literature contains many references to the problems of dispersing powders in nonaqueous liquid vehicles (1–6). Cosmetic chemists who develop pigmented formulations have to overcome flocculation, streaking, hard settling, viscosity changes and similar vexations by strictly empirical methods. Few chemists in any field can ignore pigment technology, and yet there is no single practical method based on overall theoretical concepts for evaluating this type of wetting. Quantitative data on pigment wetting efficiency, if available, could reduce the time taken up by trial and error experimentation and provide comparative information in a form which would allow selection of the most efficient components for a particular system. This study supplies such data for the first time on the wetting

*American Cholesterol Products, Inc., Edison, N.J., U.S.A.

activity of lanolin derivatives in various pigment/vehicle combinations commonly used in cosmetics.

General Considerations

Although the exact mechanism by which a surface active material aids the dispersion of pigments is not known, it undoubtedly lowers interfacial tension and promotes adsorption of the liquid vehicle on the particle surface. If effective, it also aids lubrication, mobility and plastic flow. In order to obtain desired flow characteristics, the vehicle must often be present in excess of the volume needed to just fill the void between the particles (critical pigment volume) (7).

A perfect system not only requires separation of all aggregates into discrete particles (deflocculation) but also removal of air, water and other impurities from the particle surface. A good wetting agent for pigments should function in all these respects and be effective in many different pigment/vehicle combinations.

When thoroughly wet, a powder will be dispersed as individual particles rather than aggregates. These particles will then settle slowly to a compact dense mass which will be difficult to resuspend. By contrast, a nonwetted powder will disperse as aggregates which will settle more rapidly and will attain a larger equilibrium volume. It has been suggested that an ideal dispersing agent would wet the particles to permit easy dispersion, then partially flocculate them to retard settling and promote a softer sediment for easier resuspension (8).

A search of the literature revealed several laboratory methods for obtaining data on the adsorption of vehicles on particle surfaces. A simple method was desired which could be readily employed in any cosmetic laboratory to give reliable and reproducible results on wetting efficiency. Measuring interfacial tension and contact angles, and calorimetric methods based on the heat of wetting, although valuable for basic physical chemical studies, are difficult to carry out and require specialized equipment. Microscopic examination, sedimentation tests and particle size determinations (Hegman gauge) are also useful, but these do not supply the quantitative data desired. The Daniel method for determining wet and flow points (8, 9), although developed for the paint industry, has been used on a limited basis for cosmetic materials (6). This test appeared most promising and was studied in detail.

The wet point measures the amount of vehicle needed to just wet all of the pigment. Reduction of the wet point by an additive indicates initial

surface wetting by that agent in that pigment/vehicle combination. The flow point measures the amount of vehicle needed to produce pourability. The extent to which the flow point of a pigment/vehicle system is reduced by a surface active agent measures the degree to which the agent deflocculates the system. A low wet point, coupled with a low flow point and a small difference between the two indicates good deflocculation or dispersion (8).

The Daniel method was modified somewhat to fit the requirements of cosmetic systems. The results obtained were analysed to establish validity and accuracy. Microscopic observations and sedimentation studies were employed as auxiliary measures of dispersing activity. The revised method proved satisfactory, and was used to obtain the data reported on wet points and flow points.

Test Methods

Wet Point

Equipment

10 ml burette, graduated in 0.05 ml intervals.

Glass plate, at least 8″ × 8″.

Spatula with stainless steel blade, 4″ × $\frac{5}{8}$″.

Procedure

Weigh 2.00 ± 0.01 g of powder on to a watch glass. Weigh the additive on top of the powder. Transfer the combined powder and additive to the glass plate, making sure that all the additive is transferred. Incorporate the additive into the powder by rubbing the mixture against the glass plate with the spatula. Add the vehicle dropwise from the burette, working thoroughly with the spatula after each addition. The entire mixing should take between 10 and 15 min to ensure homogeneous and complete wetting. The end point is reached when just enough vehicle has been incorporated into the powder to form a coherent mass which does not break or separate (*Figs. 1* and *2*). Record the exact volume of vehicle added.

Calculation:

Multiply the ml of vehicle added by 50 to convert to the Wet Point expressed as ml/100 g.

Precision:

The sharpness of the end point varied somewhat depending on the

powder, vehicle and additive employed. The following ranges of deviation were encountered with the systems tested :

	Av. Error	*Std. Dev.*
Replicates, one operator, same day	± 0.2 to ± 0.3	± 0.3 to ± 0.7
Replicates, two operators, different days	± 0.7 to ± 1.2	± 0.9 to ± 1.6

The degree of precision which could be attained was limited by the sample size and the size of the burette. The burette delivered 0.02 ml per drop, a difference of 1 unit in the wet point for a 2 g sample. For more precise determinations, a larger sample size and/or a smaller burette should be used.

Flow Point

Equipment:

50 ml burette, graduated in 0.10 ml intervals.
100 ml disposable beakers, approximately 2¼″ × 2½″.
Spatula with stainless steel blade, 4″ × ⅝″.

Procedure:

Weigh 20 ± 0.1 g of powder into the beaker. Weigh the additive on top of the powder. Incorporate the additive into the powder by rubbing the mixture against the sides of the beaker with the spatula. Add the vehicle from the burette, rapidly at first, then dropwise as the end point is approached. Mix thoroughly with the spatula after each addition of the vehicle. The end point is reached when just enough vehicle has been added so that the mixture flows in a uniform stream from the spatula (*Figs. 3* and *4*). Record the exact volume of vehicle added.

Calculation:

Multiply the ml of vehicle added by 5 to convert to the Flow Point expressed as ml/100 g.

Precision:

The sharpness of the end point varied slightly depending on the powder, vehicle and additive employed. The following ranges of deviation were encountered with the systems tested :

	Av. Error	*Std. Dev.*
Replicates, one operator, same day	± 1.0 to ± 4.8	± 1.4 to ± 6.8
Replicates, two operators, different days	± 2.9 to ± 3.3	± 4.1 to ± 4.6

Figure 1
Titanium dioxide/mineral oil – just prior to wet point

Figure 2
Titanium dioxide/mineral oil – at wet point

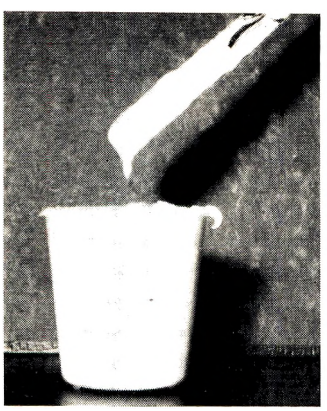

Figure 3
Titanium dioxide/mineral oil – just prior to flow point

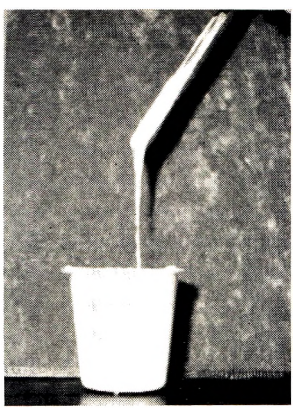

Figure 4
Titanium dioxide/mineral oil – at flow point

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Sedimentation Test

Equipment:

50 ml glass stoppered cylinders, graduated in 1.0 ml.

Volumetric flasks of sufficient size to prepare the required amount of dispersing solution.

Procedure:

Prepare a 10% w/v solution of the additive in the vehicle. Place 40 ml of this solution in the 50 ml graduated cylinder. Add 4 g of the powder. Shake the cylinder 50 times, then allow it to stand for 1 hr to aid wetting. Shake the cylinder again 50 times, then allow it to stand for 2 hr, recording the sediment volume after 10, 20, 30, 40, 60, 90 and 120 min. Shake the cylinder again 50 times, then allow it to stand for 24 hr, recording the sediment volume after 10, 20, 30, 40, 60, 90 and 120 min and after 24 hr. Record the total volume of the dispersion in the cylinder.

Calculation:

Average the sediment volumes recorded during the first 2 hr rest period with the volumes recorded at comparable time intervals during the second 2 hr rest period. For each time interval, multiply the ml of sediment by 100 and divide by the total volume in the cylinder to convert the ml of sediment to % of total volume.

Materials

Powders

Although many diverse materials are incorporated in dispersed form in make up items, four major categories are most frequently used : Extenders and carriers, opacifiers and shade lighteners, inorganic pigments, and organic pigments. One example of each of these types was selected for this investigation.

Talc (No. 141 Alpine talc, U.S.P.) is an extender and carrier for the pigments. The numerous grades available vary in purity, crystal type, particle size range, chemical composition, linseed oil absorption, etc. Acid and water levigated U.S.P. talc ground to a particle size smaller than 325 mesh was used. This talc was almost entirely hydrous magnesium silicate, containing about 1% aluminium, iron and calcium oxides. The specific gravity was 2.79, and the linseed oil absorption was 45 lb/100 lb of talc.

Titanium dioxide (No. 328 T.G.A.) increases the opacity, improves the coverage and lightens the shades of pigmented make up items. Its tendency to agglomerate makes it one of the more difficult pigments to disperse and

to maintain in a deflocculated state. Incomplete dispersion causes undesirable alteration of the shade and consistency of formulations on ageing. Titanium dioxide with a particle size less than 325 mesh was used. This grade was better than 99% titanium dioxide and met U.S.P., N.F. and T.G.A. requirements. Its specific gravity was 3.9, and the linseed oil absorption was 30 lb/100 lb of pigment.

Oxy Red (No. 3551 Pure Oxy Red) is one of a number of inorganic pigments suitable for the formulation of face and eye make ups. The pigment used contained 99% pure ferric oxide, and had a particle size less than 325 mesh. Its specific gravity was 5.18, and linseed oil absorption was 22-26.

D. & C. Red No. 9 (No. 3009 Atomic Red) is a certified organic pigment used in face make ups, rouges and lipsticks. The organic pigments are generally difficult to disperse because of their tendency to agglomerate. Red No. 9 is the barium salt of 1-(4-chloro-*o*sulpho-S-tolylazo)-2-naphthol. The pigment used had a particle size less than 325 mesh. Its specific gravity was 2.75, and linseed oil absorption was 41.6.

Vehicles

The vehicles selected represent two of the chemical types commonly used as carriers for powders in make up formulations.

Mineral oil is a mixture of nonpolar inert hydrocarbons, available in a wide viscosity range. A low viscosity (70 vis) N.F. oil was selected as typical of the grades most frequently used in cosmetics. Although it is generally more difficult to disperse cosmetic powders in mineral oil than in either *iso*propyl esters or castor oil, mineral oil is the most widely used vehicle because of its low cost.

isoPropyl palmitate is a low viscosity, slightly polar ester of a low molecular weight branched chain alcohol and a high molecular weight fatty acid. Esters of this type spread better and feel less oily than mineral oil. Cosmetic pigments are usually dispersed somewhat more easily in *iso*propyl palmitate than in mineral oil, but this ester is not used as extensively as mineral oil because of its higher cost.

Castor oil is also commonly used as a vehicle, especially in lipsticks. Initial studies, however, indicated that systems utilizing this oil as the vehicle could not be evaluated accurately by the methods described because of the high viscosities encountered at room temperature. Because it is an important vehicle, modifications of the test method are being developed in order to evaluate wetting efficiency in castor oil systems.

Additives

Twelve anhydrous, oil-miscible lanolin derivatives were selected for preliminary screening in the wet point and flow point tests. Lanolin was included for comparison. Ten of these derivatives are presently used in make up formulations; *Arlan** and *Amerchol LFA* are comparatively recent commercial developments which could be expected to prove valuable in such dispersed systems.

The derivatives tested represent diverse chemical and physical modifications of lanolin and its components as illustrated in *Table I*. All of these derivatives depress mineral oil-water interfacial tension although some of them do not emulsify this system because they lack sufficient hydrophilic-lipophilic contrast within the molecule. Each of them has other important properties which have been described in a previous publication (10).

Table I Summarized data on selected lanolin derivatives

Trade name	Generic name	Derived from			Added radical	Chemical type	Physical form	Emulsifying activity
		lanolin alcohols	lanolin acids	lanolin esters				
Acetulan	acetylated lanolin alcohols	X			acetyl	esters	thin liquid	
Amerchol L-101	multisterol extract	X				alcohols, sterols	thin liquid	X
Amerchol CAB	multisterol extract	X				alcohols, sterols	soft solid	X
Amerchol H-9	absorption base	X		X		alcohols, sterols, esters	soft solid	X
Amerchol LFA	lanolin fatty acids		X			fatty acids	plastic, firm solid	X
Amerlate P	isopropyl lanolate		X		*iso*propyl	esters	soft buttery solid	X
Arlan (11)	rearranged lanolin	X	X	X		fatty acids, esters	soft solid	X
Modulan (12)	acetylated lanolin			X	acetyl	esters	soft solid	
Polylan	lanolin alcohol linoleate	X			linoleyl	esters	viscous liquid	
Ricilan B	lanolin alcohol ricinoleate	X			ricinoleyl	esters	viscous liquid	
Ricilan C	acetylated lanolin alcohol ricinoleate	X			ricinoleyl, acetyl	esters	viscous liquid	
Viscolan	lanolin oil (dewaxed lanolin)			X		esters	viscous liquid	X
Lanolin	refined wool fat			X		esters	soft solid	X

Experimental

The concentration of additive is expressed in the data as per cent of the weight of the powder. This enables experimental evaluation to be carried

*All trade names are printed in italics.

out by varying the amount of additive while standardizing the quantity of powder. Thus the concentration of additive equals the weight in grams added to 100 g of powder.

Control measurements treating the vehicle as an additive are reported with all experimental data. Comparing the values determined for any test additive with the values reported for the same per cent vehicle control provides a direct measure of the activity of the derivative by eliminating the natural depressing effect produced by the additional vehicle in the system. The control points fall on a straight line which can be extrapolated from the weight-volume relationships determined by the specific gravity of the vehicle. Extrapolated values are enclosed in parentheses.

Preliminary Screening

In the initial study, the effect of lanolin and of the twelve lanolin derivatives on the wetting of titanium dioxide in mineral oil was explored. The concentration of additive was standardized at 10% of the weight of the powder. This represents a minimal level for cosmetic preparations since it is equivalent to 1% of a formulation containing 10% total pigments. In actual practice, lanolin derivatives are often used at concentrations as high as 10% of the finished product. Wet points, flow points and microscopic evaluation data for this series are summarized in *Table II*.

All the lanolin derivatives tested at 10% of the weight of titanium dioxide improved the dispersion of this pigment in mineral oil. However,

Table II Preliminary screening of additives at 10% concentration; wetting of titanium dioxide in mineral oil

Additive	Wet point	Flow point	Flow point-Wet point	Microscopic examination at flow point
None	57.0	270.5	213.5	flocculated
Mineral oil	44.0	(258)	(214.5)	flocculated
Acetulan	34.3	242.4	208.1	partly dispersed
Amerchol L-101	29.5	238.4	208.9	partly dispersed
Amerchol CAB	35.0	229.6	194.6	partly dispersed
Amerchol H-9	27.5	103.0	75.5	partly dispersed
Amerchol LFA	25.0	45.6	20.6	dispersed
Amerlate P	22.8	60.7	37.9	dispersed
Arlan	24.5	54.0	29.5	dispersed
Lanolin	26.0	43.6	17.6	dispersed
Modulan	30.8	45.7	14.9	dispersed
Polylan	29.5	137.1	107.6	partly dispersed
Ricilan B	36.0	136.4	100.4	partly dispersed
Ricilan C	27.5	165.8	138.3	partly dispersed
Viscolan	25.0	46.0	21.0	dispersed

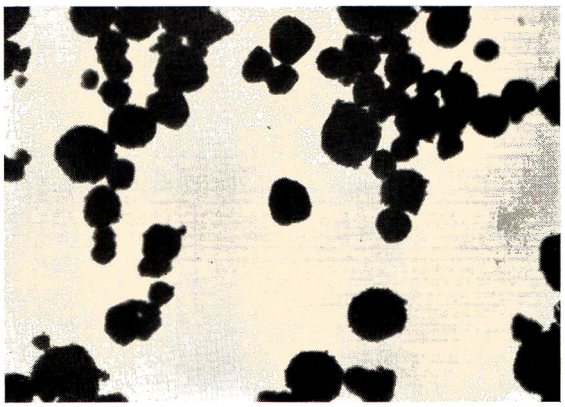

Figure 5
Titanium dioxide/mineral oil – flocculated at flow point, magnification 100X

Figure 6
Amerlate P/titanium dioxide/mineral oil – dispersed at flow point, magnification 100X

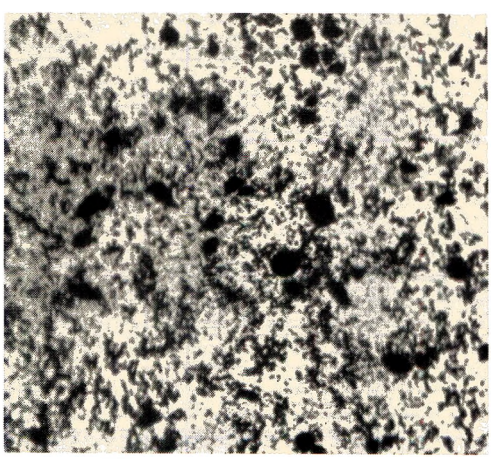

Figure 7
Acetulan/titanium dioxide/mineral oil – partly dispersed at flow point, magnification 100X

considerable variation in effectiveness was detected. Although significant reduction of the wet point was obvious in all test samples, reduction of the flow point ranged from slight, e.g. *Acetulan*, to extensive, e.g. *Modulan*. Microscopic examination of the flow point dispersions revealed that the control test was completely flocculated with no discrete particles visible (*Fig. 5*). Those dispersions with flow points below 100 were completely dispersed, as illustrated in *Fig. 6*. The partial dispersion noted in the majority of the flow point determinations is illustrated in *Fig. 7*.

While this type of screening test does not lend itself to extensive interpretation, some generalizations can be made. At equivalent concentrations in this system, the greatest effects were noted with those derivatives containing either free or esterified lanolin fatty acids (*Table I*). The comparable efficiency of lanolin and *Modulan* indicated that acetylating the hydroxyl group on the lanolin hydroxyester did not materially alter the activity in this pigment-vehicle system. *Ricilan B* and *Ricilan C*, esters which also differ from each other in free hydroxyl content, showed similarly equivalent dispersing activity.

Effect of Varying the Concentration of Additive

It was apparent that testing only one concentration of an additive might not present an accurate evaluation of its effectiveness as a dispersing aid. Although some of the derivatives showed only a slight effect on the flow point in the screening test, microscopic examination indicated significant dispersing activity. The effect of varying the concentration of additive was therefore explored in the same titanium dioxide-mineral oil system. For this series, two derivatives which did not appear to be near their optimum efficiency at 10% (*Acetulan* and *Amerchol L-101*) and two derivatives which showed substantial activity at this concentration (*Amerlate P* and *Viscolan*) were selected. Lanolin was again included for comparison. Results of these tests are detailed in *Tables III* and *IV*.

These data clearly illustrate that an additive should not be considered useless in a particular system simply because it is relatively ineffective in a single test concentration. A dramatic decrease in the flow point of the *Acetulan* and *Amerchol L-101* dispersions occurred between 10% and 15% additive concentration. Microscopic examination confirmed that dispersion in these 15% samples was complete. A lesser decrease was noted with increasing concentrations of the other additives, and all exhibited a tendency to level off around 20% additive. The wet points continued to

decrease with increasing concentrations of all additives, exhibiting no comparable levelling-off tendencies. As the wet points continued to decrease while the flow points levelled off, the difference between these two measurements reached a minimum, then started to increase. This may indicate an optimum concentration and greater amounts of additive may not materially improve wetting efficiency.

Amerlate P, *Viscolan* and lanolin, all containing esterified lanolin fatty acids, were particularly effective in this system, even at low concentrations. However, the wet point and flow point dispersions containing *Viscolan*

Table III Effect of varying concentration of additives on the wet point of titanium dioxide in mineral oil

Concn. of additive	Mineral oil (control)	*Acetulan*	*Amerchol L-101*	*Amerlate P*	*Viscolan*	Lanolin
0.0%	57.0	57.0	57.0	57.0	57.0	57.0
2.5	—	—	—	36.0	36.0	37.0
5.0	50.5	47.3	46.5	28.3	32.0	31.0
10.0	44.0	34.3	29.5	22.8	25.0	26.0
15.0	41.0	21.3	18.3	20.0	17.0	18.0
20.0	36.0	14.0	11.5	15.5	12.5	14.5
25.0	33.5	9.0	5.0	7.0	4.5	7.5

Table IV Effect of varying concrntration of additives on the flow point of titanium dioxide in mineral oil

Concn. of additive	Mineral oil (control)	*Acetulan*	*Amerchol L-101*	*Amerlate P*	*Viscolan*	Lanolin
0.0%	270.5	270.5	270.5	270.5	270.5	270.5
2.5	(267.5)	—	—	93.0	94.0	107.6
5.0	(264.5)	247.8	264.0	78.3	50.3	49.0
10.0	(258.5)	242.4	238.4	60.7	46.0	43.6
15.0	(252.5)	31.5	51.0	55.8	25.0	30.8
20.0	(246.5)	33.5	46.5	50.9	26.0	31.8
25.0	(240.5)	26.5	56.0	51.0	32.3	31.3

and lanolin were excessively sticky and stringy. Some dilatency was observed during the test manipulations of the systems containing these two additives. This might prove troublesome in actual use. In both tests, the *Acetulan*, *Amerchol L-101* and *Amerlate P* dispersions were smooth, non-tacky and elegant in appearance even at maximum additive concentrations.

Effect of Varying the Powder

Three of the derivatives which had demonstrated dispersing activity for titanium dioxide in mineral oil were evaluated as dispersing aids for three additional powders in that vehicle. Results of the wet point tests conducted on varying concentrations of these additives in the resulting 12 systems are detailed in *Table V*. Flow point data obtained on the same systems are listed in *Table VI*. Sedimentation tests were performed at an additive concentration of 100% of the weight of the powder to provide supplementary data. Results of these tests are presented in *Tables VII-X*. Control data for mineral oil are included in each table.

Titanium dioxide: The wet point and flow point data for this pigment were discussed above, but the data are included in *Tables V* and *VI* for comparison. The sedimentation tests confirmed the effectiveness of the three derivatives as dispersing aids for titanium dioxide in mineral oil, and indicated that *Amerlate P* was generally more active.

Talc: The wet point data from *Table V* indicated that the talc was wetted more readily than the titanium dioxide by mineral oil, and only slight activity was noted for the three derivatives. Substantial reduction of the flow point was accomplished by *Amerlate P*, but relatively little activity was exhibited by *Acetulan* and *Amerchol L-101* in this test. All appeared effective in the sedimentation test, but this may be due to the higher ratio of additive to pigment.

Table V Effect of three derivatives on the wet point of four powders in mineral oil

Additive and concn.		Titanium dioxide	Talc	Oxy Red	Red No. 9
Mineral oil (control)	0.0%	57.0	45.6	49.5	42.5
	5.0	50.5	38.5	43.0	37.5
	10.0	44.0	33.0	37.5	32.5
	20.0	36.0	22.5	(26.0)	(23.0)
Acetulan	5.0	47.3	34.5	40.0	38.0
	10.0	34.3	28.0	29.5	32.0
	20.0	14.0	15.0	7.5	17.5
Amerchol L-101	5.0	46.5	32.5	36.5	32.0
	10.0	29.5	25.5	29.5	27.5
	20.0	11.5	18.0	7.0	16.0
Amerlate P	5.0	28.3	35.0	21.5	40.0
	10.0	22.8	27.0	11.0	35.0
	20.0	15.5	18.0	3.0	19.5

Table VI Effect of three derivatives on the flow point of four powders in mineral oil

Additive and Concn.		Titanium dioxide	Talc	Oxy Red	Red No. 9
Mineral oil (control)	0.0%	270.5	271.2	135.6	119.9
	5.0	(264.5)	(265.2)	(129.6)	(113.9)
	10.0	(258.5)	(259.2)	(123.6)	(107.9)
	20.0	(246.5)	(247.2)	(111.6)	(95.9)
Acetulan	5.0	247.8	230.6	133.4	108.7
	10.0	242.4	198.0	128.8	98.1
	20.0	33.5	184.0	108.9	85.9
Amerchol L-101	5.0	264.0	195.2	124.5	110.4
	10.0	238.0	173.8	112.7	105.1
	20.0	46.5	165.0	57.5	82.5
Amerlate P	5.0	78.3	156.5	64.1	106.5
	10.0	60.7	126.5	43.2	93.4
	20.0	50.9	105.5	34.7	80.5

Table VII Effect of three derivatives on sedimentation rate of titanium dioxide in mineral oil

Settling time	Settling volume (% of total)			
	No derivative	*Acetulan*	*Amerchol L-101*	*Amerlate P*
10 min	35.0	100.0	100.0	100.0
20 ,,	35.0	92.5	95.0	100.0
30 ,,	35.0	50.0	83.3	100.0
40 ,,	35.0	47.5	78.8	95.0
60 ,,	35.0	43.8	68.8	91.3
90 ,,	34.3	40.0	55.0	81.3
120 ,,	33.8	37.5	42.5	74.5
24 hr	30.0	37.5	25.0	47.5

Table VIII Effect of three derivatives on sedimentation rate of talc in mineral oil

Settling time	Settling volume (% of total)			
	No derivative	*Acetulan*	*Amerchol L-101*	*Amerlate P*
10 min	93.9	100.0	100.0	100.0
20 ,,	85.4	97.6	100.0	100.0
30 ,,	78.0	97.6	98.8	100.0
40 ,,	76.8	97.6	98.3	100.0
60 ,,	73.2	96.6	97.6	98.8
90 ,,	69.5	95.1	95.8	97.6
120 ,,	67.1	92.7	94.6	96.6
24 hr	48.8	34.6	35.4	43.9

Table IX Effect of three derivatives on sedimentation rate of Oxy Red in mineral oil

Settling time	Settling volume (% of total)			
	No derivative	*Acetulan*	*Amerchol L-101*	*Amerlate P*
10 min	19.5	100.0	100.0	100.0
20 ,,	18.8	100.0	100.0	100.0
30 ,,	18.8	100.0	100.0	100.0
40 ,,	18.8	100.0	100.0	100.0
60 ,,	18.8	100.0	100.0	93.8
90 ,,	18.8	100.0	100.0	72.5
120 ,,	17.5	100.0	100.0	67.5
24 hr	16.3	17.5	18.8	40.0

Table X Effect of three derivatives on sedimentation rate of Red No. 9 in mineral oil

Settling time	Settling volume (% of total)			
	No derivative	*Acetulan*	*Amerchol L-101*	*Amerlate P*
10 min	98.8	98.8	100.0	100.0
20 ,,	96.9	97.6	98.8	100.0
30 ,,	92.7	95.1	95.1	100.0
40 ,,	92.7	93.4	92.7	98.8
60 ,,	90.9	90.2	89.9	98.8
90 ,,	80.5	85.4	82.9	98.8
120 ,,	73.2	80.5	78.0	95.1
24 hr	21.9	19.5	24.4	53.7

Oxy Red: As one might expect, this ferric oxide pigment showed some similarity in behaviour to titanium dioxide with one notable exception. Although *Acetulan* showed high activity in the flow point test at 15% of the titanium dioxide, it was relatively ineffective at 20% of the Oxy Red in this test. Again, *Amerlate P* was more active than the other two derivatives, showing good activity even at a concentration as low as 5%. The sedimentation test data exhibited the same pattern as the wet point and flow point data.

Red No. 9: At the concentrations tested, none of the derivatives demonstrated reductions in wet point and flow point with this organic pigment comparable to those shown with the inorganic powders tested. Since there appeared to be slight activity at the 20% additive concentration, it is possible that higher ratios of additive to pigment would be effective. The sedimentation tests also indicated that this may be the case. In these tests, *Amerlate P* appeared to be more active than the other two derivatives.

Effect of Varying the Vehicle

To determine the effect of the vehicle on the dispersing activity of the

derivatives, wet point, flow point and sedimentation tests were conducted on the same 12 systems tested in the previous series, substituting *iso*propyl palmitate for the mineral oil. These data are summarized in *Tables XI–XVI.*

Titanium dioxide: Although the titanium dioxide had a lower wet point in *iso*propyl palmitate than in mineral oil, no differences in the efficiency of the derivatives were noted between the two vehicles. In the flow point tests, *Amerlate P* exhibited the same pattern in both vehicles – a sharp decrease at 5% with lesser decreases at the higher concentrations. Although *Acetulan* and *Amerchol L-101* demonstrated better activity in the flow point at 5% and 10% levels in *iso*propyl palmitate than in mineral oil, these two derivatives again showed a dramatic decrease in this test between 10% and 20%.

Table XI Effect of three derivatives on wet point of four powders in *iso*propyl palmitate

Additive and concn.		Titanium dioxide	Talc	Oxy Red	Red No. 9
I.P.P. (control)	0.0%	52.3	46.8	41.5	35.3
	5.0	43.0	40.5	34.5	31.0
	10.0	35.5	35.0	27.5	25.0
	20.0	(23.0)	(25.0)	(16.5)	(14.0)
Acetulan	5.0	38.0	35.5	28.5	29.0
	10.0	32.5	22.5	21.0	22.5
	20.0	12.4	18.0	5.5	10.5
Amerchol L-101	5.0	40.0	39.5	27.5	32.8
	10.0	26.5	31.0	19.5	25.5
	20.0	12.3	11.5	4.5	15.5
Amerlate P	5.0	28.5	37.0	19.5	30.5
	10.0	24.5	31.5	13.0	22.5
	20.0	12.5	12.5	2.5	13.0

Table XII Effect of three derivatives on flow point of four powders in *iso*propyl palmitate

Additive and concn.		Titanium dioxide	Talc	Oxy Red	Red No. 9
I.P.P. (control)	0.0%	194.4	215.3	124.6	96.5
	5.0	(188.4)	(209.3)	(118.6)	(90.5)
	10.0	(182.4)	(203.3)	(112.6)	(84.5)
	20.0	(170.4)	(191.3)	(100.6)	(72.5)
Acetulan	5.0	176.3	210.4	102.5	88.8
	10.0	139.0	198.2	84.8	83.1
	20.0	34.2	177.5	32.4	68.3
Amerchol L-101	5.0	155.3	197.0	79.9	94.5
	10.0	135.4	183.0	56.2	88.5
	20.0	62.4	154.8	46.7	71.3
Amerlate P	5.0	76.0	155.9	58.5	87.6
	10.0	67.2	134.5	49.6	79.4
	20.0	61.5	104.7	41.4	70.9

Table XIII Effect of three derivatives on sedimentation rate of titanium dioxide in *iso*propyl palmitate

Settling time	Settling volume (% of total)			
	No derivative	*Acetulan*	*Amerchol L-101*	*Amerlate P*
10 min	74.4	89.8	100.0	100.0
20 ,,	62.2	81.7	100.0	100.0
30 ,,	47.6	73.2	100.0	100.0
40 ,,	39.0	65.8	100.0	100.0
60 ,,	32.4	50.0	100.0	100.0
90 ,,	30.0	32.4	100.0	93.9
120 ,,	28.0	29.3	100.0	89.0
24 hr	20.7	19.5	95.1	78.1

Table XIV Effect of three derivatives on sedimentation rate of talc in *iso*propyl palmitate

Settling time	Settling volume (% of total)			
	No derivative	*Acetulan*	*Amerchol L-101*	*Amerlate P*
10 min	97.6	98.8	98.8	98.4
20 ,,	96.9	97.6	97.6	97.6
30 ,,	95.1	97.6	97.6	97.6
40 ,,	95.1	96.6	96.6	96.6
60 ,,	92.7	95.1	95.1	94.6
90 ,,	89.9	92.7	92.7	92.2
120 ,,	85.4	89.9	90.2	87.3
24 hr	41.5	36.6	29.3	39.0

Table XV Effect of three derivatives on sedimentation rate of Oxy Red in *iso*propyl palmitate

Settling time	Settling volume (% of total)			
	No derivative	*Acetulan*	*Amerchol L-101*	*Amerlate P*
10 min	78.8	78.8	100.0	100.0
20 ,,	68.8	68.8	100.0	100.0
30 ,,	60.0	55.0	100.0	100.0
40 ,,	50.0	45.0	100.0	100.0
60 ,,	37.5	22.3	100.0	100.0
90 ,,	21.3	17.5	100.0	91.3
120 ,,	21.3	17.5	100.0	90.0
24 hr	15.0	15.0	12.5	41.3

Table XVI Effect of three derivatives on sedimentation rate of Red No. 9 in *iso*propyl palmitate

Settling time	Settling volume (% of total)			
	No derivative	*Acetulan*	*Amerchol L-101*	*Amerlate P*
10 min	98.8	98.8	100.0	100.0
20 ,,	96.9	97.6	98.8	100.0
30 ,,	92.7	95.1	95.1	100.0
40 ,,	92.7	93.4	92.7	98.8
60 ,,	90.9	90.2	89.9	98.8
90 ,,	80.5	85.4	83.6	98.8
120 ,,	73.2	80.5	78.0	95.1
24 hr	21.9	19.5	24.4	53.7

In the sedimentation tests, *Amerchol L-101* and *Amerlate P* were effective in both vehicles, while *Acetulan* showed less activity in *iso*propyl palmitate than in mineral oil.

Talc: Changing the vehicle from mineral oil to *iso*propyl palmitate did not materially alter the wet point data for the control or for the additives. Although the control flow point data were lower in *iso*propyl palmitate than in mineral oil, the flow points determined for the derivatives were essentially the same in both vehicles. This may indicate reduced effectiveness in *iso*propyl palmitate. The sedimentation test data also indicated reduced activity for the derivatives in this vehicle.

Oxy Red: The wet points of the control and of the additives were lower in *iso*propyl palmitate than in mineral oil but they followed similar patterns in both vehicles. Although the control flow points were similar in both vehicles, the derivatives were more effective in *iso*propyl palmitate. At 20% additive, *Acetulan* appeared most active, even though it was relatively ineffective in mineral oil. The sedimentation test data did not indicate this dispersing activity for *Acetulan*, but did confirm the effectiveness of *Amerchol L-101* and *Amerlate P*.

Red No. 9: The test data in *iso*propyl palmitate paralleled the data determined in mineral oil.

Discussion

All the test procedures revealed significant pigment wetting and dispersing activity for lanolin derivatives. The wet point and flow point measurements provided quantitative data which could be used to determine efficient additive/pigment ratios for each system. Sedimentation tests, conducted at higher additive concentrations, and microscopic examination

of the flow point dispersions, although in themselves neither definitive nor quantitative, proved valuable supplementary procedures.

In several instances, an additive flow point had approximately the same numerical value as the control. Microscopic examination of these dispersions revealed that the additive sample was partly deflocculated and the control was completely flocculated. This indicated that the additive should be explored further at higher concentrations. Microscopic examination thus anticipated the sharp drops in the wet points and flow points of the mineral oil/titanium dioxide dispersions containing *Acetulan* and *Amerchol L-101*. Such sharp drops probably represent reaching the critical ratio of pigment/additive/vehicle required for complete dispersion.

Similarly, the sedimentation test often indicated activity for systems which appeared comparatively inactive in preliminary wet point and flow point measurements. This was noted with the *Amerlate P*/Red No. 9 combination and indicated the advisability of continuing the tests at higher additive concentrations.

In the titanium dioxide/mineral oil system, lanolin and its liquid fraction demonstrated good wetting and dispersing properties. However, the dispersions were tacky and stringy. Potentially troublesome dilatency was also noted. By contrast, all the other lanolin derivative dispersions were smooth and elegant and handled easily in all test manipulations. Thus the chemically modified derivatives retained the desirable wetting action while eliminating the inherent disadvantages of lanolin.

The initial screening tests on the titanium dioxide/mineral oil system indicated that those derivatives containing free or esterified lanolin fatty acids were the most active dispersing aids. The lanolin fatty acids consist of normal, branched and hydroxy acids having a wide range of molecular weights. Because of their unique chemical configuration, these fatty acids exhibit functional properties vastly different from those of conventional fatty acids. This is clearly demonstrated by the superior performance of *Amerlate P* (*iso*propyl lanolate) in contrast to the inactivity manifested by *iso*propyl palmitate.

No overall rating of relative efficiency can be made for pigment wetting and dispersing agents because of the many criteria by which efficiency may be judged. An ideal agent would achieve complete dispersion at a low additive to pigment ratio in a minimal amount of vehicle and would be active in many systems. Because of the specific action of wetting additives, the ideal dispersing aid may well be found in a combination of surface active materials.

Until this ideal dispersing agent or combination of agents is found, the most efficient additive for any application must be the one that meets the primary dispersing requirements of each individual system. If the lowest possible ratio of additive to pigment is the most important consideration, then a derivative such as *Amerlate P* would be utilized. If, on the other hand, the primary requirement is a system containing a minimal amount of vehicle, then an additive which gives the lowest flow point should be selected. *Acetulan*, which gave exceptionally low flow points at slightly higher additive concentrations, would be the preferred dispersing aid. The type of data presented in this study can be used to make such selections.

It is possible that further investigations now being conducted on a broader range of materials, including homologous series, may disclose underlying concepts relating chemical structure to dispersing action. Furthermore, analysis of a greater volume of data may allow reliable prediction of wetting activity based on established patterns of behaviour.

Summary and Conclusions

Modified wet point and flow point procedures are described. Their validity as quantitative measurements of the wetting and dispersing activity of lanolin derivatives in several cosmetic pigment/vehicle systems is demonstrated. The value of the sedimentation test and microscopic examination of the flow point dispersions was illustrated.

All the lanolin derivatives evaluated by the described tests exhibited significant wetting and dispersing action. This activity was found to be specific so that data obtained in any additive/pigment/vehicle system could not be applied to another system differing by even one component. Similarly, neither the effective level of wetting aid nor the volume of vehicle required to reach a desired result could be predicted.

Of the derivatives studied in some detail, *Amerlate P* was the most versatile, demonstrating wetting and dispersing activity at relatively low concentrations in mineral oil and *iso*propyl palmitate for the three inorganic pigments. There were indications that concentrations of *Amerlate P* higher than 20% would achieve dispersion of the organic colour. While *Amerlate P* (*iso*propyl lanolate) exhibited excellent activity, *iso*propyl palmitate showed very little activity in the combinations tested.

Acetulan demonstrated generally good wetting activity with some specificity for pigments and vehicles. No pattern was observed which could explain or predict this specificity.

Amerchol L-101 exhibited definite dispersing activity for the two metal oxides in both vehicles and showed modest activity for talc. The effect of *Amerchol L-101* was insignificant in dispersing the organic colour.

Lanolin derivatives provide the formulation chemist with effective pigment dispersing aids which have valuable moisturizing, conditioning and emollient effects as well. Evaluating them by the described methods simplifies the problem of selecting the derivative which will be most effective for a specific pigment/vehicle system.

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DISCUSSION

MR. E. W. CLARK: In the experiment on sedimentation rate the most effective additive appeared to be *Amerlate P*. This is a solid substance and presumably increased the viscosity of the mineral oil. Is it possible that this increased viscosity, as opposed to a dispersing effect, was at least partially responsible for the slower sedimentation?

MR. CONRAD: Yes, it is possible. We have tried lanolin in the same series and in other series which we have not presented here, and *Amerlate P* seemed to be quite different from lanolin in its effect. The *Amerlate P* is a soft solid; the melting point does not differ much from that of lanolin, just one or two degrees higher.

MR. E. W. CLARK: In the *Tables* you were comparing *Amerlate P* with two other derivatives, and the other derivatives were thin liquids, so there would be a considerable difference in viscosity.

MR. CONRAD: Yes.

DR. B. A. SCOTT: Is the chemical nature of these lanolin derivatives sufficiently well defined to assess cross-sectional diameters? If this is the case, plotting per cent weight of additives rather than fraction of surface covered at any concentration may explain differences between lanolin derivatives.

MR. CONRAD: The materials listed cover a cross-section of all types of lanolin derivatives. Some of these are esters, some are extracts of alcohols containing hydrocarbons, some of them are acetates of alcohols. There is a range of molecular weight, lanolin itself being anywhere from 700 to 1000 depending on the presence of diesters. Some of the lower weight esters are around 350. You have a difference in molecular weight, you have quite a difference in viscosity, and you have quite a difference in consistency. These are all factors, there is no question about it. Here we are trying to present a general method for comparative use in wetting.

Mr. J. G. PITT: I would have thought that the wetting effect of these lanolin derivatives would be proportional to concentration in the vehicle rather than relative to the weight of powder. When the flow point test is done and a dispersed suspension obtained, does the powder reflocculate when the full dilution with vehicle is carried out?

MR. CONRAD: We tried this in one or two cases, but it seemed to be a concentration effect. A minimum critical concentration of additive is probably required to prevent reflocculation.

BRITISH CHEMICAL REFERENCE SUBSTANCES

In late 1963, the General Medical Council and the Pharmaceutical Society of Great Britain agreed to set up a joint authority to prepare and distribute chemical reference substances needed to carry out certain tests and assays described in the British Pharmacopoeia, the British Pharmaceutical Codex and the British Veterinary Codex. The Joint Committee held its first meeting in March 1964, and established a number of panels. Each panel was charged with the task of establishing one or more of these reference substances, and, since these substances might be of value for other purposes, the panels were asked, should it prove impracticable to obtain absolute purity, to ascertain as far as possible the amounts of all impurities.

The first two British Chemical Reference Substances are now available – Digoxin and 2-t-butyl-4-methoxyphenol (the most active isomer present in butylated hydroxyanisole). The 2-t-butyl-4-methoxyphenol *Reference Substance* is required for the assay of butylated hydroxyanisole and in the IR identification test. In this case, a purity of at least 99.85 per cent has been achieved, the balance being made up of very small amounts of 3,3′-di-(t-butyl)-2,2′-dihydroxy-5,5′-dimethoxybiphenyl (bis-BHA), 2,5-di(t-butyl)-4-methoxyphenol, 4-methoxyphenol and a trace of an unidentified impurity. As well as its pharmaceutical uses, butylated hydroxyanisole has extensive usage in the food industry as an antioxidant in oils and fats, and the establishment of this reference substance may be welcomed in fields outside of pharmacy.

Samples of these reference substances are distributed by the Pharmaceutical Society and are available on application to the Assistant Director, Department of Pharmaceutical Sciences, 17 Bloomsbury Square, London, W.C.1, at a cost of £3 for 0.2 g of the 2-t-butyl-4-methoxyphenol.

2-t-BUTYL-4-METHOXYPHENOL

The batch of 2-t-butyl-4-methoxyphenol constituting the Reference Substance was prepared for the Joint Committee by May and Baker Ltd. from commercial material of good quality by fractional distillation *in vacuo*, followed by passage of a solution in chloroform through alumina and removal of the solvent from the eluate.

The Reference Substance has the following general analytical characteristics:

Description: A slightly cream-coloured crystalline powder with a characteristic odour.

Sulphated ash: Less than 0.05 per cent.

Volatile impurities (determined as the loss in weight in a partial vacuum for 3 hours): Less than 0.01 per cent.

Melting-point: 64.1°.

Thin-layer chromatographic test (British Pharmacopoeia 1963, Addendum 1964): No spots detectable other than that due to 2-t-butyl-4-methoxyphenol.

Infra-red spectrum (British Pharmacopoeia 1963, Addendum 1964): Complies with test.

Ultra-violet spectrum: In a mixture of 49 parts by volume of dehydrated alcohol, B.P., and 1 part by volume of N hydrochloric acid, a 0.002 per cent w/v solution shows maxima at 228 mμ (E1 per cent, 1 cm = 340) and 292 mμ (E 1 per cent, 1 cm = 205) and a minimum at 253 mμ (E1 per cent, 1 cm = 8).

The possible impurities in the Reference Substance, which are unlikely to be revealed by the above tests at the level of purity expected of the material, were hydroquinone, 4-methoxyphenol, 3-t-butyl-4-methoxyphenol, 2-5-di-(t-butyl)-4-methoxyphenol (di-BHA) and 3,3′-di-(t-butyl)-2,2′-dihydroxy-5,5′-dimethoxybiphenyl (bis-BHA). The Reference Substance was therefore examined more critically by thin-layer chromatography and gas-liquid chromatography.

Thin-layer chromatography. The system used was that described in the B.P. 1963, Addendum 1964, which is based on that of Seher(1). At the loading required in the B.P. monograph (0.2 mg), only the spot due to 2-t-butyl-4-methoxyphenol was detectable. When the loading of the Reference Substance was increased to 1 mg, a spot corresponding with that of bis-BHA was detectable in addition and estimated as equivalent to 0.01 per cent in one laboratory and 0.02 per cent in a second. In one laboratory, a spot corresponding with that of di-BHA was just detectable and estimated at 0.01 per cent or less. No spot corresponding with hydroquinone, 4-methoxyphenol or 3-t-butyl-4-methoxyphenol was detectable by either laboratory; the contents of these impurities (if present at all) in the Reference Substance were thus assessed as less than 0.01 per cent, less than 0.02 per cent and less than 0.1 per cent, respectively. When estimating the concentrations of the impurities present from inspection of these thin-layer chromatograms, it was appreciated that the absence of the main constituent, or the presence of varying amounts of it, may give rise to modified spot areas, leading to false evaluation.

Gas-liquid chromatography. The Reference Substance was examined using the conditions detailed below, which gave maximum sensitivity with the apparatus used.

Sample size: 10μl of a solution containing 1 g of Reference Substance in 1 ml of benzene.

Column: 12 ft glass U-tube containing the 60–80 mesh fraction of 60–100 mesh, acid-washed *Embacel* kieselguhr impregnated with 15 per cent w/w of *Embaphase* silicone oil.

Column temperature: 180°C.

Inlet temperature: 310°C.

Carrier gas: Hydrogen.

Detector: Flame-ionisation.

With this system, 3-t-butyl-4-methoxyphenol, hydroquinone and bis-BHA are not detectable. 4-Methoxyphenol and di-BHA are detectable at levels of 0.002 per cent and 0.005 per cent, respectively (by peak-area comparison), but were not detected in the Reference Substance. One unidentified impurity (not revealed by hin-layer chromatographic examination) was detected however in the Reference Substance and was estimated as about 0.001 per cent (expressed as 4-methoxyphenol).

CONCLUSION. From these tests, it is concluded that the British Chemical Reference Substance 2-t-butyl-4-methoxyphenol contains not less than 99.85 per cent of 2-t-butyl-4-methoxyphenol, together with a total of not more than 0.15 per cent of impurities, all but one of which have been characterised.

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Book reviews

LECTURE NOTES ON DERMATOLOGY. B. Solomons. Pp. viii + 249 + Ill. (1965). *Blackwell Scientific Publications, Oxford.* 21s.

The author's preface states that this is an introduction to dermatology for students and general practitioners. Dr. Solomons would not have been much concerned with its value to cosmetic chemists but this review is naturally influenced in this direction. There is no question of whether the book is a useful guide to "do-it-yourself" dermatology for chemists; this is not so much to be eschewed through subservient reverence for the closed shop of medicine as in recognition of the absolute necessity for clinical experience as a background to proper appreciation of a medical text. Lacking such experience, is there any benefit to be gained by a chemist reading a dermatological textbook? Within certain limits, your reviewer believes that there is indeed.

To conduct research on or to manufacture cosmetics, it is surely vital to have some idea of the good and bad effects that products exhibit on the skin; insofar as unfavourable reactions may be coincidental or directly related to the topical application, the investigator ought to have some notion of the possible consequences and of the indications for calling upon expert clinical advice. Studying the relevant sections of a fairly elementary book on dermatology, such as Dr. Solomons', will create the right attitude of mind.

It would be presumptuous for a non-medical reviewer to criticize the strictly clinical aspects of this book, but various physiological matters or descriptions of topical treatments are relatively easy to assess. For example, the list of allergens on page 84 is hardly comprehensive but it is doubtless selected for its practical significance. The typical dogma or over-simplification characteristic of a smallish handbook is seen in the statement on page 51 referring to cosmetics "there is no article amongst these substances which cannot produce a dermatitis" or on page 129 which states baldly that tinea versicolor is a fungus infection "due to Microsporum furfur." On page 71, there is the statement that seborrhoeic dermatitis of the scalp is basically an increase in the normal amount of scaling of the epidermis, which is known as dandruff; expression of the relationship in this manner is at least of dubious validity.

Dr. Solomons' book is, as suggested above, concisely written in a style avoiding obscure and highly specialized phraseology. It is well produced and has an exceedingly fine collection of photographic illustrations.

ESSAYS IN BIOCHEMISTRY. Vol. 1. Editors: P. N. Campbell and G. D. Greville. Pp. xi + 170 + Ill. (1965). *Academic Press, London and New York.* 18/6.

This is the first of a projected series of volumes containing essays on biochemical topics. The audience for which the book is designed comprises mainly

advanced students, but it is hoped also to interest teachers dealing with parts of biochemistry in which they are not expert, and research workers wishing to obtain an up-to-date picture of topics outside their speciality.

The first essay, "The role of CO_2 fixation in metabolism," (H. G. Wood and M. F. Utter) deals with the nature and significance of enzymes from heterotrophic cells capable of forming a carbon-carbon bond from CO_2 and an acceptor molecule. The discussion covers the role of biotin, and evaluates the significance of the fixation reaction in gluconeogenesis, fatty acid synthesis, and the metabolism of propionate.

"On the mechanism of muscular contraction" (R. E. Davies) covers a very complex topic firstly with a historical introduction and a description of the micro-anatomy of muscle and activating and relaxing factors, then with energy relationships, and finally summarizes a postulated molecular mechanism which accounts for many of the phenomena observed during muscle contraction.

"Sequence determination in nucleic acids" (K. Burton) discusses methods currently being used in a field which has lagged behind achievements in sequence analysis of proteins, but which it is hoped will soon yield complete sequences of some of the smaller RNA's.

"Oxidative phosphorylation" (D. E. Griffiths) describes the advances that have been made in the last few years in the study of the respiratory chain in mitochondria, and the associated conservation of bond energy in ATP.

"The biochemist's green mansions: The photosynthetic electron transport chain in plants" (R. E. Hill) deals with the energy relationships in photosynthesis, and traces the historical development of theories to the present day when the precise linkage between photochemical activation and the reduction of CO_2 is still a point at issue.

These essays do not attempt to be complete reviews of their respective fields, but each carries an extensive list of references. They are well tailored for their declared object of aiming at students and non-specialists, being neither too elementary nor too detailed for this purpose, and stimulating the reader by describing current problems and anticipated advances.

The book carries author and subject indexes, and is printed to a high standard. The only sign of economy in this volume stated to be priced for students is the paper back, which in the reviewer's copy became detached rather easily. Otherwise it is very good value, and it is to be hoped that the Biochemical Society will be encouraged to continue the series. B. G. OVERELL.

SCHMIDT'S ORGANIC CHEMISTRY. 8th Edn. Editor: N. Campbell. Pp. xi + 941 + Ill. (1964). *Oliver & Boyd, Edinburgh and London.* 63s.

Schmidt's Organic Chemistry has a long and honourable history as an undergraduate primer – and indeed has not been found inappropriate for precocious sixth-formers. Moreover, it has always placed proper emphasis on references to original work. For this new edition, Dr. Campbell has made extensive revisions and introduced, inter alia, some treatment of reaction mechanisms, non-benzenoid aromatic hydrocarbons, conformational analysis, biosynthesis, and a few of the newer reactions and intermediates; passing reference is also made to some "chemical curiosities" that appeal to the author. He hopes thereby to supply "a standard textbook for advanced

students and a useful reference book for research workers." Whilst granting that revision and modernization of an existing complex work are not easy – and that no two chemists will agree on what should be retained and what displaced – it must be contended the book is entirely too superficial. There is pitifully little reference to physical organic chemistry and inadequate mechanistic description of reactions. Nomenclature is dismissed in less than one page and it is irritating to find outmoded conventions still employed – such as substituents denoted as 1:3:5– rather than 1,3,5– and use of the downturned phenanthrene skeleton for abietic acid.

In a preliminary general section of 103 pages, general principles are enunciated. Reference to details of ultimate analysis are properly omitted but the implication that oxygen is (still) normally determined by difference is unfortunate in a modern textbook. Useful examples are given of the deduction of empirical and molecular formulae. There is a commendable attempt to give a condensed account of electronic concepts of valency and the LCAO approach to molecular orbitals – just enough to whet the appetite but seriously in need of supplementary lectures, not necessarily too mathematical. Stereochemistry and tautomerism are moderately well described. Finally, brief reference is made to a pot-pourri of physical properties and sundry topics – such as mp, bp and distillation, colour, solubility, polarity, bond dimensions, mesomerism, optical activity, ORD (dismissed in a paragraph), nucleophilic and electrophilic substitution mechanisms, IR and UV (but not NMR and mass) spectroscopy, chromatography (column, paper and gas) and ion exchange.

The main portion of the book, like Gaul, is divided into three parts. The first part, Aliphatic Compounds, follows the conventional systematization by functional groups, simple and multiple. This catalogue of properties and reactions is enlivened by examples of applications such as fermentation processes, the diversity of petroleum products and the commercial polymerization of olefins vinyl derivatives and esters; some might regret that fluorocarbons receive only passing mention. The section on carbohydrates and polysaccharides is particularly effective. Part 2, Carbocyclic Compounds, begins with alicyclics; monoterpenes are well covered but only open chain and decalin related sesquiterpenes are considered whilst diterpenes are dismissed with the appalling statement that "comparatively little is known" of them; a passing reference is made to squalene as a triterpene. Aromatic functions are comprehensively, if superficially, covered; the interesting topics of cine substitution and benzyne bonds are merely mentioned and there is a brief factual introduction to nonbenzenoid aromatics. This part concludes with a section on steroids that compares favourably with Karrer and provides a suitable undergraduate introduction to tests such as, say, that of the Fiesers'.

The final part deals with Heterocyclic Compounds. The simpler systems are treated conventionally but the derived alkaloids are unevenly discussed – thus the vast and important realm of indole alkaloids is dismissed in a few lines whilst morphine and its congeners receive considerably more attention. Superficial coverage is given to other groups of natural products including vitamins, hormones and antibiotics, although the sections on enzymes, porphyrins and proteins are more balanced. In all three parts occasional references are made to biogenetic origins; acetate coupling (in connection with polyphenols) and mevalonic acid intermediates are briefly mentioned.

In short, Schmidt has always been a valuable undergraduate primer and Dr. Campbell has struggled manfully to modernize it, but this is too Herculean a task

for one volume. He has provided a most readable book, reasonably priced, that should whet the appetite of the intelligent undergraduate or GRIC student – but these will have to read a great deal further and need many supplementary lectures to clothe the skeleton supplied. Judged on his stated aims and against modern textbooks now available, it must be concluded – regrettably – that he has not succeeded. G. F. PHILLIPS.

INDEX TO REVIEWS, SYMPOSIA VOLUMES AND MONOGRAPHS IN ORGANIC CHEMISTRY 1961-1962. Editors: N. Kharasch and W. Wolf. Pp. ix + 260. (1964). *Pergamon Press, Oxford.* 70s.

This volume is the second in a series which should prove extremely useful to all who have to delve into the literature of organic chemistry. It lists titles of review articles published in English, French, German and English translations of Russian literature; full references to all articles are given. The first volume covered the period 1940–1960 and contained about 7,000 titles; the present volume covers the period 1961–1962 and lists about 2,500 titles.

The survey includes articles from a very wide selection of journals, periodicals, review publications, monographs – from the small to the multi-volume works, symposia and collective volumes.

A very liberal interpretation has been taken of the subject matter "organic chemistry" and the scope of the coverage can be gathered from a short list of subjects noted which are of particular interest to cosmetics and perfumery chemists: Autoxidation and antioxidants, antifungal agents, allergy, enzymology, thin-layer and other forms of chromatography, fatty acids, essential oils, surface-active agents, detergents and detergency, terpene chemistry, colouring matters, microscopy, lipid chemistry, soap, gums, design and construction of laboratories. A supplementary list of journals, etc., which are "potentially useful sources of information" is appended and this includes our own Journal. A useful addition to this list might have been its contemporary Proceedings of the Scientific Section, Toilet Goods Association. The volume concludes with comprehensive indexes to subjects and authors and a list of publishers and their addresses. This volume is very well produced; obviously great care has been exercised in its preparation and it should prove an invaluable addition to any chemical library. R. P. REEVES.

ANGEWANDTE CHEMIE. International edition in English. Monthly. Annual subscription: \$32 = £11.10.0 = DM 116. *Academic Press, Inc., London and New York, Verlag Chemie GmbH; Weinheim/Bergstr.*

For 77 years Angewandte Chemie has been publishing first class review articles and topical surveys from all fields of chemistry; although emphasis is on practical organic chemistry, the other divisions – and even theoretical aspects – receive attention. The journal is notable for the rapid publication of short communications, which for many research workers may be the first indication of progress in their particular field. Important scientific conferences, not only in Europe but also the

larger meetings elsewhere in the world, are reported and useful abstracts are culled from current issues of the principal chemical journals. The book reviews are usually well written and interesting, although they naturally tend to be concerned primarily with texts of German origin.

Since January 1965 the International Edition of Angewandte Chemie has represented a complete translation of the German edition; hitherto approximately three quarters of each issue were translated – which sometimes posed an invidious selection for the editors. Confusion sometimes arose where reference was made in the literature to only one of the two editions and many libraries only carried the English language version. In the first three years, the "growth rate" achieved a steady 10%. The interest shown by applied chemists throughout the English speaking world then led the publishers to make the International Edition a cover-to-cover translation of the German original – with a concomitant 35% increase in size. All review articles, short communications, conference reports, abstracts and book reviews appearing in the two German issues each month, are now translated and combined in a single issue published at the end of the same month.

The first review in the International Edition, appearing in January 1962, dealt with non-enzymatic synthesis *in vitro* of polysaccharide and nucleic acids and included some interesting biopoietic speculation. A very high standard has been consistently maintained; for instance, earlier volumes this year have reviewed in detail the correlation of mass spectra, the configuration and sequence observed in polymers, strained ring compounds and two aspects of illumination mechanisms. The conference reports are remarkably informative and yet concise – not normally considered to be a Teutonic attribute! Thus the January number described congresses of biochemistry, photochemistry, gas chromatography, organic sulphur compounds, coordination compounds, peptides, lignin and minerals; it may be significant that all but the last are essentially organic chemical topics.

For the presentation of high calibre reviews and reports alone, this journal is warmly to be commended; that the publishers are able now to offer a cover-to-cover full translation for the original price constitutes a remarkable bargain.

G. F. PHILLIPS.

HOW TO FIND OUT IN CHEMISTRY. C. R. Burman. Pp. vii + 220. (1965). *Pergamon Press, Oxford.* 17/6.

This is a new volume in the Technical Information series of the Commonwealth and International Library. It is intended to provide a career guide for personnel officers, an indication of literature sources for the student and to remind research workers of standard texts within and beyond their discipline. The first get brief but comprehensive guidance, the second more thorough direction whilst the third may find use for this book. The key to the customer most likely to find profit lies in a passing reference in the preface to "students of librarianship" – in fact the whole book reads like a part of their course. This opinion is supported by the bibliological questions appended to each chapter. It is not surprising therefore to find that the book is compiled by the Liverpool Technical Documentation Officer and Librarian. The style is necessarily highly compressed and factual but the author's smooth prose renders it readily readable.

A few points of criticism must be made. Inclusion in a Commonwealth series

is somewhat misleading in that virtually all the reference works are from UK and USA, with other European countries a poor third. The first Commonwealth reference was found on page 40 – a useful librarian's text book from Melbourne – and four Commonwealth countries are mentioned in the list of societies in chapter 11. Although nominally published this year, it is to be regretted that few of the reference works cited postdate 1962 and organizational changes have since taken place in some of the bodies listed; in this type of publication, proof insertion – if necessary by footnote – should have been possible. The index is barely adequate and there is an almost total lack of cross reference between individual chapters; casual reading might suggest an omission only remedied by careful scrutiny elsewhere.

The book is organized into 12 chapters. The first is a useful concise summary of training and careers in chemistry, primarily from the UK stand-point; the function of the RIC is well covered. Some readers might not agree with the statement that the successful student will find "many interesting and well paid openings in industry, government service and teaching"! A rather dry chapter summarizes the organization of libraries and their classification and catalogue procedures. The next chapter is entitled "Guides" and is concerned with national bibliographies and catalogues, with particular reference to mammoth American collations; for journals with book lists and reviews, only four US and two UK are somewhat arbitrarily mentioned. Most of the better known chemical and technical encyclopaedias are quoted and biography, history and personal directories are not overlooked. Chapter 4 is an introduction to the various types of periodicals – general, polyvalent, industrial and specialist and translations of originals. Some readers may be confused by the reference to the existence of nearly 100,000 scientific and technical titles and then – pious hope – to be enjoined to read original papers to see what work supported the published abstract. A most important chapter describes the nature, purpose, scope and indexing of abstracts and lists the principal journals in which these may be found. Special attention is given to the construction and use of *Chemical Abstracts*; reproductions illustrate specimen portions of the list of journals covered, general text and subject and formula indexes. The leading German, British, Soviet and French abstract services are described. A useful section briefly introduces the novice to systematic searching of the chemical literature. Five more chapters consider the periodicals, serial reviews, monographs, treatises, data and methods collections, and a selection of comprehensive text books, special to General and Physical, Analytical, Inorganic and Organic Chemistry and Chemical Technology respectively. The particular literature of crystallography, spectroscopy, chromatography, polarography and electrophoresis, trade terms and the principal technical polylingual dictionaries, are also dealt with. The diversity of international, British, Commonwealth, US and specialist societies, science unions, research councils, professional associations, industrial organizations and research institutes, are well reviewed in Chapter 11. It is noted that both the US and the UK Societies of Cosmetic Chemists each merit a paragraph but CSMA and BAMA are not mentioned. The final chapter itemizes a variety of US and British government publications including reports and guides; special sections deal with atomic energy, patents and standards organizations.

This might well be described as an annotated super bibliography or a chemists' source book. It is in the form of a pocket book and is reasonably priced.

G. F. PHILLIPS.

AN INTRODUCTION TO CHEMICAL NOMENCLATURE

R. S. Cahn. 2nd. Edn. Pp. x + 109 (1964). *Butterworths, London.* 13/6.

Chemical nomenclature is a vital subject which is the centre of continuous controversy and confusion. In part, the confusion must be due to the sketchy and scattered treatment given to nomenclature by most chemical textbooks. There is, therefore, a real need for Dr. Cahn's book.

The treatment he gives to nomenclature in the three main divisions of chemistry is in justifiable contrast. Physical chemistry is covered by a four-page list of standard physicochemical symbols recommended by the Symbols Committee of the Royal Society (1951). A 28-page chapter is devoted to inorganic chemistry. The basis is the International Union of Pure and Applied Chemistry (I.U.P.A.C.) 1957 Nomenclature Rules, together with Chemical Society and Chemical Abstract Usage. The full coverage given by this chapter gives it value both as an introduction and as a handy reference to inorganic nomenclature.

Inevitably the attention given to organic nomenclature is longer (55 pages), more complex and less complete. The treatment is divided into five chapters; General; The Principal Functional Group; Building a Name; Skeletal Types; Some Special Cases. The approach throughout is rightly "synthetic", i.e. building up a name from a structural formula; deriving the formula from the name will follow naturally from this. Again the basis is the I.U.P.A.C. 1957 Rules with Chemical Society and Chemical Abstract usage. Attention is drawn throughout to contrasting American and European convention. (Minor changes have been made in this edition of the book to take account of the I.U.P.A.C. 1961 Tentative Rules.) This section reveals adequately that organic nomenclature is in a state of flux and that there is not, necessarily, a unique, "correct" name for a given compound, but it does this without confusing the underlying principles. It is in this section of the book that the word "Introduction" properly applies. Information on more specialized topics such as terpenes, steroids and carbohydrates is understandably left to references. However, an explanation of prefixes such as syn-, anti-, endo-, exo-, neo-, allo- is, perhaps, a less justifiable omission.

The major change in this edition is the addition of a 13-page chapter of worked exercises – a section that will, undoubtedly, prove of value not only to the student. The style and length of the whole book make it easy to read and any chemical library should benefit by its presence. R. N. BEVITT.

CHROMATOGRAPHIC REVIEWS, VOL. 7. M. Lederer, ed.

Pp. viii + 202 + Ill. + advertisements (1965). *Elsevier Publishing Company, Amsterdam/London/New York.* 60s.

Reference was made in a notice of Volume 6 (1) to the broadening of the original ambit of this series. Dr. M. Lederer has continued this trend; there are three articles summarizing progress in the application of paper partition (p.p.c.) to highly specialized topics, two monographs reviewing novel extensions of chromatographic procedures and an account of thin layer (t.l.c.) techniques in a particular field of natural product chemistry.

L. R. Snyder, from the Californian oil industry, examines in detail the theoretical

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principles of gradient elution, stressing that there is no very fundamental distinction from conventional stepwise variation of eluent. The main practical advantages are elimination of uncertainty in determining when (stepwise) changes ideally should be made and the avoidance of spurious peaklets where this point has been misjudged. He then reviews the considerable literature regarding the choice of apparatus and techniques and concludes a lengthy account with general advice for selecting an optimum compromise among elution conditions. A glossary of preferred symbols and an extensive bibliography are appended.

J. P. Adloff, a French radiochemist, discusses successively radiochromatographic applications of gas phase (previously reviewed by him in Volume 4), paper partition, electrophoretic, adsorption and ion exchange separations, for the study of a very comprehensive series of products of the Szilard-Chambers effect, i.e. the chemical or kinetic resultants of nuclear recoil reactions.

The first volume included a review of chromatographic separation of chloroplast pigments published prior to 1959; Z. Sestak of the Czech Academy of Science brings up to date p.p.c. methods for chlorophyll and carotenoids. He refers to other reviews and relevant portions of handbooks, to suitable types and treatment of paper, to the manner of application of solutions, to the development of apparatus and new devices, to a variety of solvent systems, to factors influencing separation and to interesting applications. However, the main bulk of the article comprises a remarkably detailed tabulation of published adsorption, reverse phase and more specialized methods for separating chloroplast pigments. It remains to be seen whether the paper techniques reviewed therein are going to be superseded by t.l.c. procedures.

The introduction (1955) of two-dimensional p.p.c. constituted a great step forward for plant biochemistry; V. H. Booth (Cambridge) describes the contribution this technique has made in his and other hands to the separation and simultaneous display of a wide variety of known and unidentified fat soluble plant products. With obvious enthusiasm and a chatty style, the author summarizes the discoveries – and some of the pitfalls – in the elucidation of lipid structures. He admits that some of his conclusions are speculative and draws attention to gaps in our knowledge of lipid distribution and function. Curiously he does not seem to consider t.l.c. when indicating future development.

V. Betina (Bratislava University) presents an extremely comprehensive review of the great contribution that p.p.c. has made to the elucidation of antibiotics, particularly the means to characterize many new ones and to demonstrate identity of some that have been independently isolated. Antibiotics belong to many diverse groups of organic structures, having little in common save their biopotency – which, however, does permit the development of bioautographic detection procedures. General aspects are considered first and then the results with better known antibiotics; a great variety of chromatographic methods of classification are tabulated followed by an indication of aids in the search for new metabolites. There are tables of numerous solvent systems, many diagrams illustrating, for instance, the variation of R_f with pH and altogether 578 references are cited.

The close association and low concentration of steroids render efficient separation essential; t.l.c. is now one of the most important analytical procedures. E. Heftmann (U.S. Dept. of Agriculture) assesses the relative advantages of t.l.c. and other separation methods; thus g.l.c. may generally be more accurate and convenient for quantitative analysis but non-specific detectors require preliminary t.l.c. or liquid column

separation. He discusses the choice of supports, solvents and detection techniques. Examples are given of the separation of the individual sterols, sapogenins, alkaloids, bufotoxins, bile components, cortical hormones, androgens and estrogens.

Republication of lectures this year has been avoided; all six articles have been written specially for this number – several of them by earlier contributors. Despite an overall 10% reduction in the number of pages compared with previous volumes in this series, the average length of individual reviews has increased slightly. Judged as a critical survey of progress and diversification of chromatography in specific fields over the past several years, the high standard set by preceding reviews has been skilfully maintained. G. F. PHILLIPS.

Society of Cosmetic Chemists of Great Britain

1965 DIPLOMA EXAMINATION

Brunel College

PAPER I

(Monday, 21st June 1965.)

Candidates should answer FIVE questions from *not less than FOUR* sections.

SECTION A

1. Why do molecules absorb light of various wavelengths? Define and give examples of chromophoric and auxochromic groups. Describe the effect of increasing the number of chromophoric and auxochromic groups in an organic molecule.

2. Write notes on *three* of the following:
   (a) Reactions between thioglycolate and human hair.
   (b) Extensometer tests on human hair.
   (c) Solvent assisted dye mechanisms.
   (d) Brushless shaving creams.

SECTION B

3. Give a brief account of the colouring materials used in eye make-up. Describe the various types of eye-shadow currently available, illustrating with formulae. Discuss the advantages and disadvantages of each type of eye-shadow.

4. Discuss the formulation of a modern lipstick. In particular, define the desirable characteristics which you would attempt to achieve and difficulties which you might expect to encounter in your development programme. Indicate how a basic formula can be modified to give it
   (a) improved application

(b) increased creaminess

(c) increased gloss on the lips

(d) greater suitability for tropical sale.

Section C

5. Indicate what factors you would consider in choosing a polythene squeeze pack for an alcoholic hair spray. Describe how you would assess these factors in order to make sure that the pack would function well, and that an adequate shelf life would be obtained.

6. Describe what you would look for in developing a pack for an aerosol deodorant. Discuss briefly, both those factors which influence the performance, and those which affect its shelf life.

Section D

7. Give a general account of the anatomy of the bacterial cell and explain fully the importance of the wall and cytoplasmic membrane.

8. What are the important bacteria found on the skin? Describe the part played by these organisms in the production of body odour and discuss the problems involved in the selection of a germicide for incorporation in a body deodorant.

Section E

9. Describe the principal types of contact dermatitis and distinguish carefully between them.

10. What general procedure would you follow in formulating skin creams? Illustrate your answer with reference to the following products:

Hand creams.

Cleansing creams.

Foundation creams.

Sunscreen creams.

PAPER II

(Wednesday, 23rd June 1965.)

Candidates should answer FIVE questions from *not less than FOUR* sections.

SECTION A

1. What are the principal differences between lyophobic and lyophilic colloids?

   A solution containing 1.2×10^{-2} equivalents/l of dissociated non-diffusible carboxymethylcellulose is equilibrated across a semipermeable membrane with a solution containing 6.0×10^{-3} mole/l of sodium salicylate. The membrane allows free passage of the salicylate ion. Calculate the ratio of salicylate on the two sides of the membrane at equilibrium.

2. Describe the practical and theoretical details of the Maximum Bubble Method for the determination of surface tension.

   How does this method compare with other methods commonly used for the measurement of surface tension?

SECTION B

3. Discuss the autoxidation of long-chain materials and its relation to the development of rancidity in toilet products. Describe protective methods used in final products and outline the manner in which various treatments of raw materials can have a useful combating effect.

4. Describe the properties of long-chain materials that are useful in cosmetic preparations. Describe the structure and outline the way in which these materials such as oils and fats, waxes, petroleum products, silicones are effective for different purposes.

SECTION C

5. Discuss the characteristic advantages of
   (a) liquid chromatography, and
   (b) gas-chromatography
   as separation methods. Give examples of applications of these methods which you consider to be of importance to cosmetic chemists.

6. What is meant by the Beer-Lambert law? Give a brief description of a spectrophotometer suitable for making transmission measurements of solutions in the visible spectrum, and outline how it could be used to determine the concentration of a coloured substance present in a solution.

Section D

7. Describe as fully as possible how two important series of perfumery raw materials are obtained from citronella and lemongrass oils. Indicate briefly how these raw materials can now be manufactured by alternative synthetic processes.

8. (i) Discuss the problems encountered in formulating suitable perfumes for

   (a) toilet soaps,
   (b) lipsticks,
   (c) aerosols.

   (ii) Suggest one simple basic formula of at least four constituents for a rose and for a jasmin perfume.
   Include if possible an approximate indication of the proportions of those constituents mentioned.

Section E

9. State, with reasons, for what type of rheological measurement the Ostwald (U-tube) viscometer is suitable and describe the experimental procedure you would follow in using it to determine the viscosity of a given liquid.

10. "Emulsions are thermodynamically unstable." Discuss this statement with reference to creaming, flocculation, coalescence and inversion.

Successful Candidates

Ten out of seventeen candidates were successful. Diplomas were awarded to the following:

S. R. Ahmad	W. A. de Alwis	D. C. Unsworth
*Miss H. C. Birrell	E. H. Dudman	J. A. Watts
W. T. Charville	Miss M. Markogiannis	U. Wickramasekera
	R. S. Phillips	

*£5 prize.

1965-66 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.

2nd December 1965

The selection of scientific personnel

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

6th January 1966

The economics of research

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

3rd February 1966

Perfumery lecture

(Jointly with British Society of Perfumers)

31st March 1966

Some aspects of laboratory planning

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

FILM EVENING: Thursday, 19th May 1966.

MEDAL LECTURE: Thursday, 3rd March 1966.

The changing face of organic chemistry

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

1966 DINNER AND DANCE: Saturday, 5th February 1966, at the Europa Hotel, Grosvenor Square, London, W.1.

ANNUAL GENERAL MEETING: Monday, 23rd May 1966, at the Washington Hotel, Curzon Street, London, W.1.

SYMPOSIUM ON PHYSICAL METHODS

A Symposium on Physical Methods will be held at The Grand Hotel, Bristol, on the 16th and 17th November 1965. (For details see *J.* p. 484.) Registration forms are available from the General Secretary, Mrs. D. Mott, 18 Warner Close, Harlington, Middx. *The closing date for registration is 18th October 1965.*

SYMPOSIUM ON COLOUR

A Symposium on Colour will take place in Eastbourne, Sussex, during the week commencing 25th April 1966. *Programme Secretary:* Mr. S. J. Bush, Muter & Hackman, 325 Kennington Road, London, S.E.11.

SYMPOSIUM ON PRODUCT TESTING

A Symposium on Product Testing will take place in Royal Leamington Spa, Warwickshire, on 16th November 1966. *Programme Secretary:* Mr. N. J. Van Abbe, Beecham Toiletry Division Ltd., Great West Road, Brentford, Middx.

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