VOL XVII NO 4 1 APRIL 1966

Journal of the Society of Cosmetic Chemists

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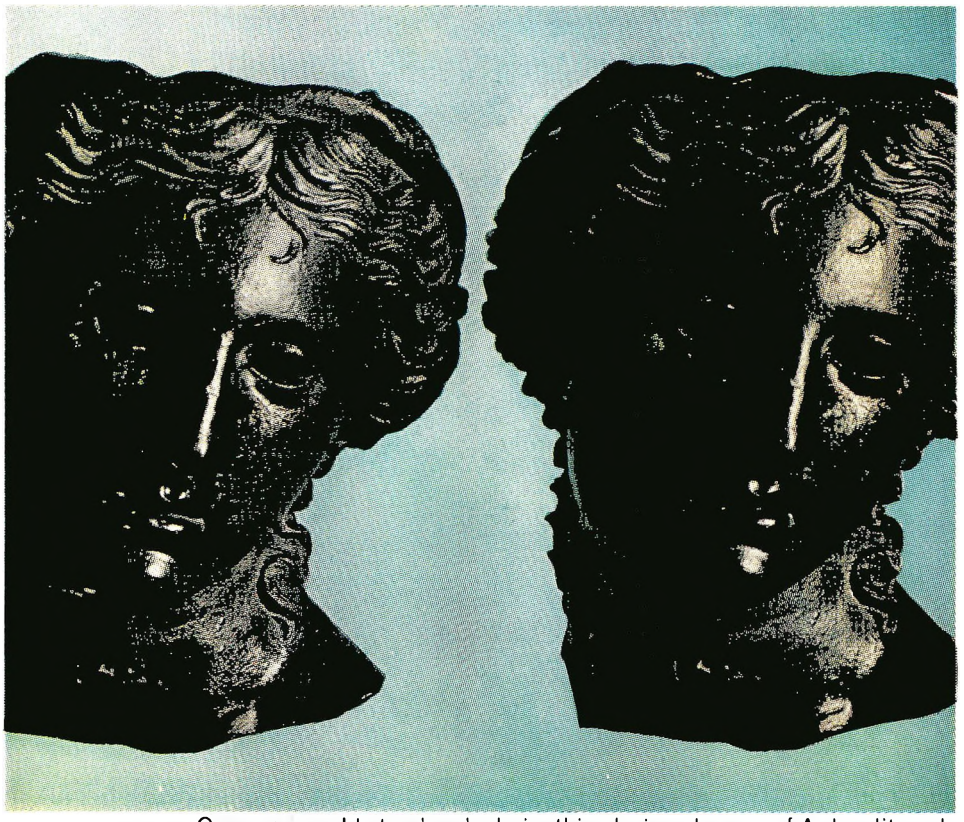

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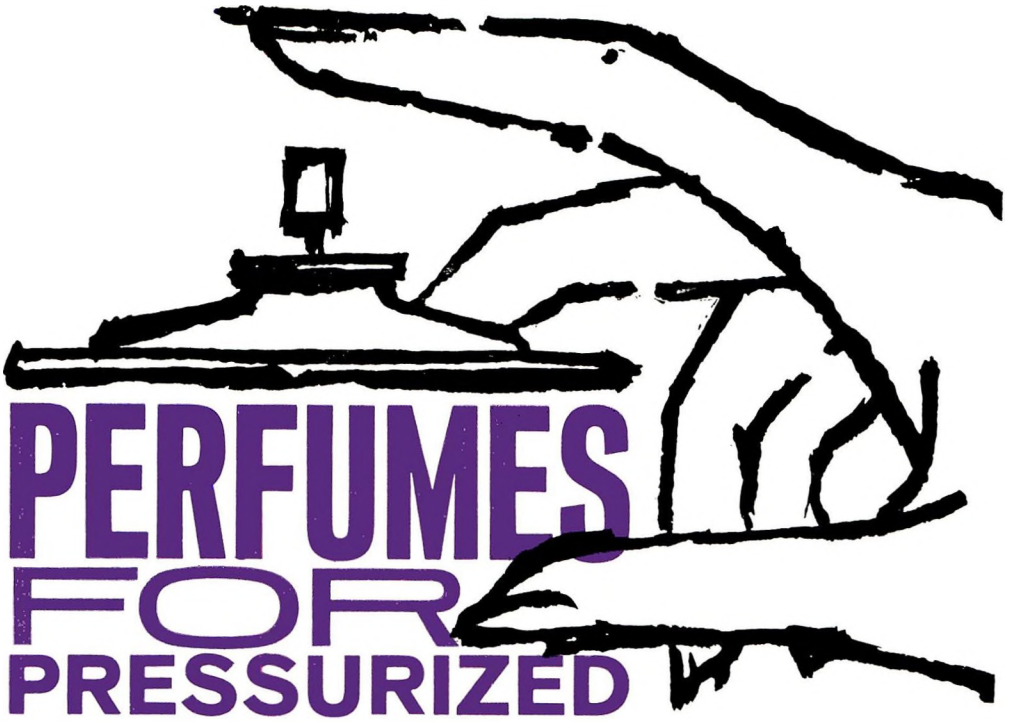

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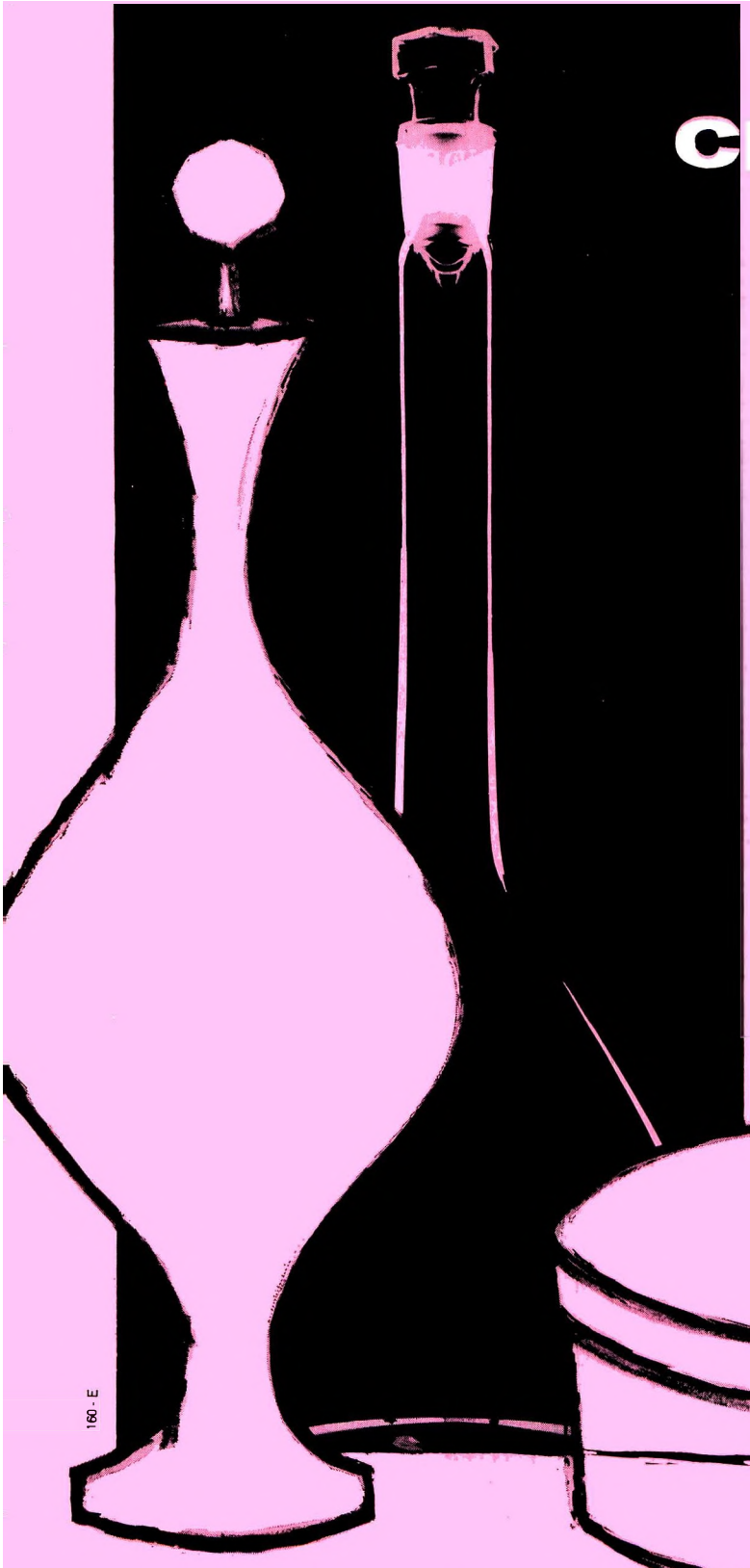

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SYNOPSES FOR CARD INDEXES

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

Turbidimetric method for the rapid evaluation of antimicrobial agents: M. R. W. BROWN.
Journal of the Society of Cosmetic Chemists **17** 185-195 (1966)

Synopsis—A rapid, economical method of evaluating antimicrobial activity is described which uses turbidimetric measurement of log phase cultures. Two new preservatives, *Dioxin* and *Bronopol*, were found to be active against *Ps. aeruginosa* even in the presence of polysorbate 80. There was some evidence that the activity of *Dioxin* was increased in the presence of the polysorbate. A mixture of *p*hydroxybenzoates was shown to have enhanced activity against *Ps. aeruginosa* in the presence of 0.02% polysorbate 80 but the activity was eliminated in the presence of higher concentrations of the nonionic agent.

Particle size analysis using Coulter Counters: W. M. WOOD and R. W. LINES. *Journal of the Society of Cosmetic Chemists* **17** 197-211 (1966)

Synopsis—A relatively new instrument for the size analysis of most forms of particulate material is described. The instrument senses particles suspended in an electrolyte by their momentary displacement of electrolyte, causing an increase of resistance to applied current, as each passes through a small hole, or orifice, in an insulator. Passage is essentially singly, although corrections can be applied for any coincidence loss. Counts at up to 5,000 particles per second are possible, and the resulting size distribution is built up in some twenty minutes, including calculation time, although this can be reduced on a routine basis.

A technique for the size analysis of wide range powders, i.e. those wider than the range of resolution of any particular orifice, is discussed.

The range of new models available working on this same basic principle is reviewed. These reduce calculation time considerably, as well as incorporating many other refinements.

A series of particle size distribution on a wide range of cosmetic materials illustrate the usefulness and versatility of the instrument.

Rheological studies of new cream bases with the Brookfield Synchro-Lectric viscometer: F. NEUWALD.
Journal of the Society of Cosmetic Chemists **17** 213-233 (1966)

Synopsis—The Fryklöf method for studying plastic systems, using the Brookfield Synchro-Lectric viscometer with T-shaped spindles, is reported. Rheological studies of o/w creams show the suitability of the instrument and the Fryklöf method for plastic systems, e.g. pharmaceutical and cosmetic ointments and creams. Rheograms were constructed from which the yield value and the plastic viscosity could be calculated and from which, in addition, the occurrence of thixotropy or rheodestruction could be observed.

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J. Soc. Cosmetic Chemists **17** 185-195 (1966)

Turbidimetric method for the rapid evaluation of antimicrobial agents

Inactivation of preservatives by nonionic agents

M. R. W. BROWN*

Presented at the Symposium on "Physical Methods," organised by the Society of Cosmetic Chemists of Great Britain, in Bristol on 16th November 1965.

Synopsis—A rapid, economical method of evaluating antimicrobial activity is described which uses turbidimetric measurement of log phase cultures. Two new preservatives, *Dioxin* and *Bronopol*, were found to be active against *Ps. aeruginosa* even in the presence of polysorbate 80. There was some evidence that the activity of *Dioxin* was increased in the presence of the polysorbate. A mixture of *p*hydroxybenzoates was shown to have enhanced activity against *Ps. aeruginosa* in the presence of 0.02% polysorbate 80 but the activity was eliminated in the presence of higher concentrations of the nonionic agent.

Introduction

There is an extensive literature about photoelectric methods of measuring concentrations of bacterial suspensions (1,2). The purpose of this paper is to describe one method which has certain useful features and to give results of the application in measuring antibacterial activity in the presence of a nonionic surface active agent. The procedure is economical of time, materials and technical assistance.

A bacterial culture during the log phase is relatively homogeneous and each cell is actively metabolising and dividing at about the same rate. Consequently, if a chemical agent is added to a culture in the log phase then any change in growth rate may be attributed to the action of the agent (3,4).

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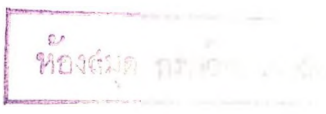


The turbidity of a bacterial suspension is due predominantly to the scattering of light passing through the suspension. This scattering occurs mainly at the cell surface because of the high refractive index gradient between the medium and the cell surface (5).

The method described here is based upon measurement with a spectrophotometer of the reduction of light transmitted using *Pseudomonas aeruginosa* cultures growing in the presence of a nonionic surface active agent.

Nonionic agents are known to antagonize the action of many chemical preservatives (6–8). The antagonism depends upon several factors including the concentration of nonionic agent. Brown and Richards (4,9) found that 0.02% polyoxyethylene sorbitan mono-oleate (polysorbate 80) present in the growth medium made *Ps. aeruginosa* sensitive to the action of benzalkonium chloride, chlorhexidine diacetate and polymyxin B sulphate. However, 0.5% polysorbate 80 eliminated the antibacterial action of the benzalkonium and chlorhexidine but not that of the polymyxin.

The purpose of the present study was to investigate further the activity of various chemical preservatives in the presence of different concentrations of polysorbate 80.

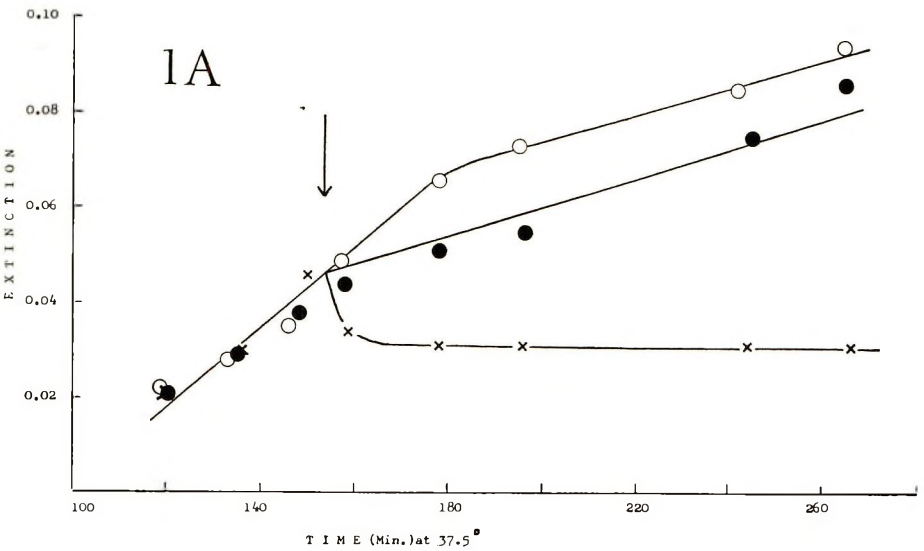
Experimental

The test organism was *Pseudomonas aeruginosa* NCTC 8203 and Oxoid nutrient broth No. 1 was used as the basic medium. The incubation and reaction temperature was 37.5°. Replicate agar slants were inoculated using a broth culture from an isolated colony. The slants were stored frozen, and a fresh slant was used for each experiment. Logarithmic growth rates were followed by measuring the absorbance at 420 mμ with a *Unicam 600* spectrophotometer. Microscopic examination of the culture was also made. Antibacterial agents used were a mixture of 2 parts methyl *p*hydroxybenzoate and 1 part propyl *p*hydroxybenzoate, *Dioxin* (6-acetoxy-2,4-dimethyl-*m*-dioxane) and *Bronopol* (2-bromo-2-nitropropane 1,3-diol).

Effect of antibacterial agents on growth rate

The method of Brown and Garrett (3) was used to reduce any lag phase to a minimum. Prewarmed broth was inoculated from an overnight culture and the absorbance was measured at intervals. At a predetermined value, such that the cells were known to be dividing exponentially, replicate inocula were taken and added separately to prewarmed broth containing zero, 0.02% and 1% polysorbate 80. Each concentration was in triplicate.

Every culture was allowed to grow until it was at a convenient point in the log phase when two of the three replicates were inoculated with 0.5ml of a solution of the antibacterial agent. Simultaneously the remaining culture was inoculated with 0.5ml of the solvent as a control. The antibacterial solutions and the control solvents were added slowly to the cultures which were briefly shaken during the addition. This procedure eliminated temporary changes in absorbance resulting from vigorous addition of liquid to the growing cultures (9). The solvent for *Dioxin* and *Bronopol* was water, that for the *p*hydroxybenzoates was 70% alcohol. The absorbance of each culture was measured at intervals and results with *Dioxin* (0.03% and 0.1%), *p*hydroxybenzoates (0.03% and 0.1%) and *Bronopol* (10 μg/ml and 100 μg/ml) are illustrated in *Figs. 1–3* respectively.



Results and Discussion

Dioxin

The presence of polysorbate 80 at each concentration apparently had no antagonistic effect upon the activity of *Dioxin*. *Fig. 1* shows the effects in plain broth and broth with 1% polysorbate 80. 0.03% *Dioxin* caused a slight inhibition of growth rate in each case and 0.1% *Dioxin* caused an immediate lysis, slightly greater in the culture with 1% polysorbate 80. The results with 0.02% polysorbate 80 (not illustrated) were substantially the same as with 1% polysorbate 80.

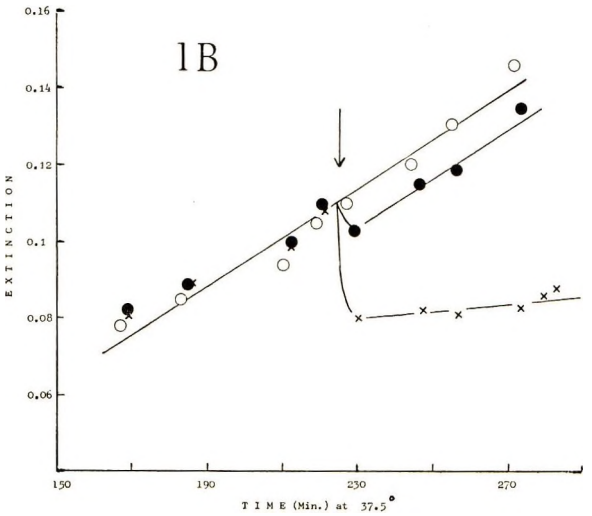
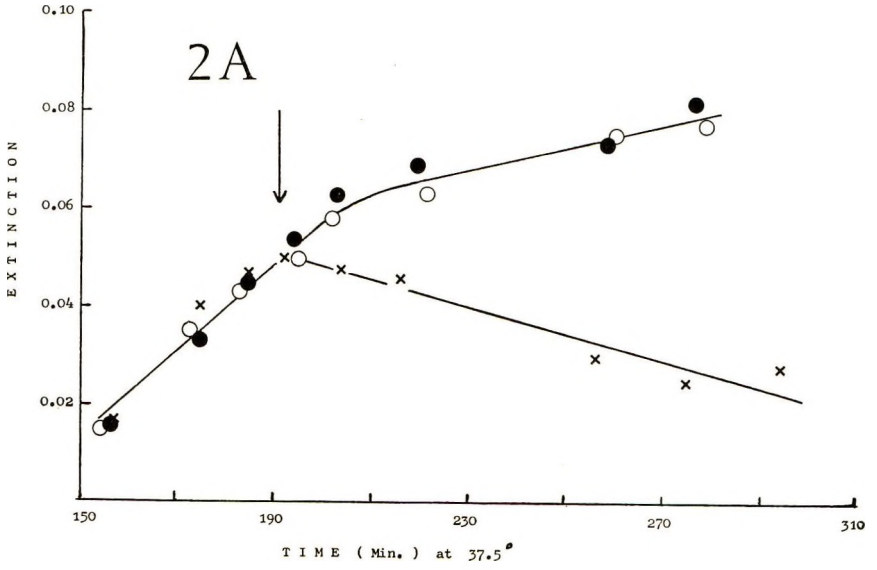


Fig. 1 Effect of polysorbate 80 on the action of *Dioxin* against log phase cultures of *Ps. aeruginosa*.

○ control.
● *Dioxin* 0.03% added.
× *Dioxin* 0.1% added.
A, plain broth. *Dioxin* added after 154 min.
B, broth with 1% polysorbate 80. *Dioxin* added after 225 min.



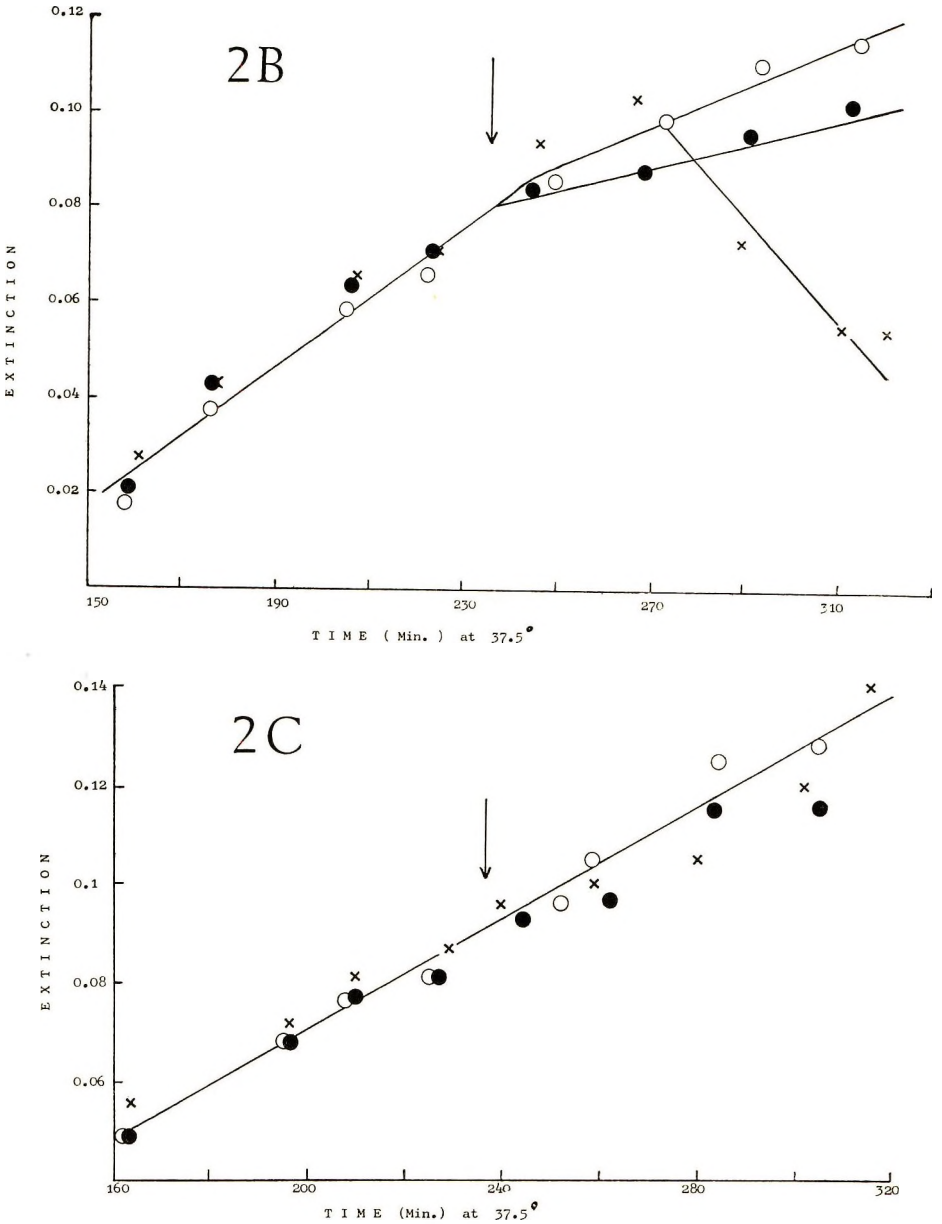


Fig. 2 Effect of polysorbate 80 on the action of *p*hydroxybenzoate mixture against log phase cultures of *Ps. aeruginosa*.

○ control.
● 0.03% *p*hydroxybenzoates added.
× 0.1% *p*hydroxybenzoates added.
A, plain broth. *p*Hydroxybenzoates added after 191 min.
B, broth with 0.02% polysorbate 80. *p*Hydroxybenzoates added after 236 min.
C, broth with 1% polysorbate 80. *p*Hydroxybenzoates added after 237 min.

*p*Hydroxybenzoates

There was no appreciable effect upon the growth rate in plain nutrient broth when *p*hydroxybenzoate to produce a concentration of 0.03% was added to the log phase culture (*Fig. 2*). 0.1% *p*hydroxybenzoate, however, immediately reduced the growth rate to zero and some lysis occurred.

The effect of 0.03% *p*hydroxybenzoates in the presence of 0.02% polysorbate 80 was slightly to reduce the growth rate, while 0.1% *p*hydroxybenzoate caused an immediate lysis of greater magnitude than occurred in plain broth. It appeared that 1% polysorbate 80 prevented any significant antibacterial action by either 0.03% or 0.1% *p*hydroxybenzoates. This antagonism is well known (7,10).

The apparent increase in activity with the *p*hydroxybenzoates in the presence of 0.02% polysorbate 80 and of *Dioxin* with both concentrations of polysorbate corresponds to a similar enhancement of activity of benzalkonium, chlorhexidine and polymyxin against *Ps. aeruginosa* (4). It has been suggested that the high resistance of this organism to chemical antimicrobial agents is related to its permeability properties (4,11). These properties may be changed by polysorbate 80, allowing the penetration of chemicals in low concentrations which would not enter the cell in the absence of polysorbate 80. Brown and Richards (11) have recently shown that the resistance to chemical agents of *Ps. aeruginosa* and of *Escherichia coli* has also been reduced by the action of ethylenediamine tetraacetic acid, probably by an effect on cell permeability.

Bronopol

The action of *Bronopol* on the growth rate was not significantly affected by the presence of either of the polysorbate 80 concentrations used. *Fig. 3* illustrates the effect of 10 μg/ml and 100 μg/ml *Bronopol* in the presence of plain broth and broth with 1% polysorbate 80. The results with 0.02% polysorbate 80 (not illustrated) were not significantly different from those with 1% polysorbate 80. It appears that polysorbate 80 had no significant effect upon the action of *Bronopol* against log phase *Ps. aeruginosa*. This is in accordance with the results of Croshaw *et al* (12) and Bryce and Smart (13). This method was unable to distinguish any difference between the action of 10 μg/ml and 100 μg/ml *Bronopol*. Both concentrations apparently caused slight lysis. It is possible that the higher concentration killed more cells than did the 10 μg/ml but that the extent of lysis as measured optically was not appreciably different.

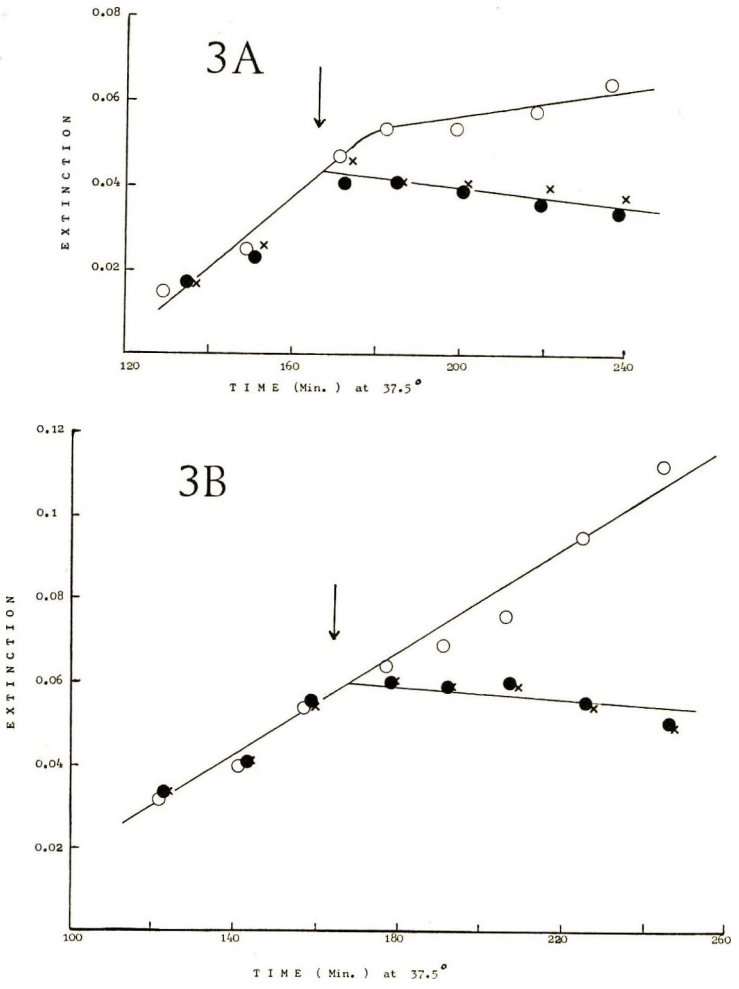


Fig. 3 Effect of polysorbate 80 in the action of *Bronopol* against log phase cultures of *Ps. aeruginosa.*

○ control.
● *Bronopol* 10 μg/ml added.
× *Bronopol* 100 μg/ml added.
A, plain broth. *Bronopol* added after 166 min.
B, broth with 1% polysorbate 80. *Bronopol* added after 165 min.

Summary and Conclusions

All the preservatives tested were active against *Ps. aeruginosa.* *Dioxin* was not antagonized by polysorbate 80. On the contrary, it appeared that its activity was slightly enhanced in the presence of polysorbate 80. The slight enhancement occurred in each of two other experiments similar

to that illustrated in *Fig. 1*. The *p*hydroxybenzoate mixture was antagonized by 1% but not by 0.02% polysorbate 80, the latter concentration apparently having some synergistic effect. This effect, shown in *Fig. 2*, was reproduced in each of two replicate experiments. The activity of *Bronopol* was unaffected by the presence of polysorbate 80 (*Fig. 3*).

The procedure described is a rapid and convenient method of assessing antimicrobial activity. It is possible for one worker to measure the growth rates of about 10 cultures and to obtain the results within one day. An apparatus based upon similar principles but recording several growth rates continuously and automatically has been described by Coultas and Hutchison (2). The method is particularly useful for preliminary screening purposes. There are, nevertheless, limitations to these procedures. Cultures are not optically dense if less than about 10^7 cells/ml and the useful concentration range for measuring growth rates by this method is about 10^7–10^8. This is a narrow range relative to that possible using colony counting methods. Furthermore, the method is not suitable in circumstances where the chemical agent significantly causes clumping. In such a case an end point method of evaluation may then be more appropriate.

ACKNOWLEDGEMENT

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Introduction by the lecturer

The main point to be made is that using the method described it is possible rapidly to assess antibacterial activity against log phase cells. Furthermore, about 10 cultures can be used at any one time so that a flexible experimental design is possible.

Unfortunately, this method is not the answer to all our desires about testing chemical antimicrobial agents. There are several limitations to the method which are mentioned in the paper. In general, it may be said that these procedures are useful, mainly for preliminary screening purposes, but are not restricted exclusively to screening. It is possible to obtain precise quantitative relationships between growth rates and to compare the effects on growth rate of such variables as chemical concentration, reaction temperature, pH and cell concentration.

DISCUSSION

PROF. F. NEUWALD: Can you give me any idea why, in *Fig. 2B*, the bacterial effect after the addition of 0.1% *p*hydroxybenzoates occurs about 30 min after the addition? In all your other *Figures*, the growth rate decreases immediately after the addition of the chemical agent.

THE LECTURER: What you say is quite true and is in fact rather interesting. For most of our work, and indeed in order for the method to be most useful, it is necessary that the conditions are such that when a chemical is added to a culture in the log phase its effects are immediately apparent. When this happens it is possible to get a quantitative relationship between the rates of growth. We have been able to show that there is a relationship between total cell numbers that are living or dead, and the viable count as well as with the optical density. In some cases, however, this does not happen, e.g. where we added 0.1% *p*hydroxybenzoates to *Pseudomonas aeruginosa* growing in the presence of 0.02% *Tween*. This particular culture had the chemical added and about 25 min later the growth curve tailed off and there was considerable lysis. Such a drop in optical density must be due to lysis unless there is some peculiar occurrence in the culture, such as clumping. This possibility was eliminated by examining the culture microscopically. Under these circumstances it is not possible to get any precise quantitative relationships between rates of growth and kill, but nevertheless from the practical point of view of preservation, I think this method can still tell us something useful. I have seen this delayed phenomenon before. It occurred when I was working with penicillin and *E. Coli* and the effect was reproducible in that it occurred but the extent to which it occurred and the length of the delay was not very reproducible. The delay in *Fig. 2B* does seem to correspond to approximately a generation time, but whether in fact this is significant I do not know.

MR. N. J. VAN ABBÉ: How does your work on the reported results relate to the usual concepts of bacteriostasis and bactericidal activity?

THE LECTURER: I find the terms bacteriostatic and bactericidal activity a source of confusion. If tetracyclin is added to *E. Coli*, the cell count is about 10^8 and one plots log numbers against time and then, depending upon the concentration added to a log phase culture, there could be a reduction in count from 10^8 to 10^2. As far as those cells are concerned, I suppose the activity has been bactericidal. If the count remained at 10^2 one would say this is acting as a bacteriostat, i.e. no growth is

occurring, yet this may be simply a function of time. If measured after three weeks one could get growth. It is acting as a bacteriostatic agent, even though possibly there has been a drop of 99.9999% and those cells are dead. I would suggest that in these circumstances, the words bacteriostatic and bactericidal are very often unhelpful. It would be better to say there has been a drop in count of six log cycles and that growth subsequently recurred.

PROF. F. NEUWALD: Have you measured or do you have any idea about the concentration of the bactericidal agent, after its addition and in the presence of *Tween 80*? I think it possible that with the higher concentration of *Tween 80*, the chemical will be bound, perhaps partly, by the *Tween 80*.

THE LECTURER: This is commonly accepted. The reason that we are getting no apparent effect upon the growth rate by the *p*hydroxybenzoate mixture is because there is no *p*hydroxybenzoate mixture there. It is bound by the nonionic. Several workers have published this, and I have given one or two references above.

At Bristol we are extremely interested in *Pseudomonas aeruginosa* and are carrying out research into the reason for its resistance from several angles. We would be very interested if anybody happened to find anything that would cast a light on this relationship.

MR. N. J. VAN ABBÉ: What happens if readings are taken for longer periods than shown in the paper?

THE LECTURER: This method, although extremely rapid and relatively easy to learn, does have several serious limitations. It is measuring optical density and records the amount of light that is not scattered. If, therefore, you are measuring a system in which the chemical kills the cell, i.e., prevents it reproducing but does not cause lysis, it might sterilize the entire culture, but if there is no lysis then all one could observe is that the optical density remains constant. With *Ps. aeruginosa* using many common preservatives such as benzalkonium, chlorhexidine, *p*hydroxybenzoates and one or two others that we have tested, lysis occurs and the optical density does quite closely correlate with total and viable counts.

MR. R. CLARK: Would you like to make a hypothesis or give some explanation why you get an apparent synergism of 0.02% polisorbate with the *p*hydroxybenzoate? You observed a similar behaviour with *Dioxin* at all concentrations.

THE LECTURER: We have found previously (4) that in the presence of 0.02% polysorbate 80, the activity of benzolkonium, chlorhexidine and polimyxin were all enhanced. If the concentration of polysorbate was increased, the polymyxin was always enhanced. There appeared to be synergism. The activity of the chlorhexidine and the benzalkonium decreased as the concentration of nonionic increased. Thus we had the usual and expected result that polysorbate 80 will bind with these chemicals and eliminate them biologically from the system. We do have a hypothesis to explain this. We think that *Ps. aeruginosa* is exceptionally resistant to chemicals because of its permeability properties, and the polysorbate 80 is affecting the permeability properties to such an extent that chemicals get in which are normally kept out. In the case of the benzalkonium and the chlorhexidine the situation is complicated by the fact that not only is the polysorbate making the cells more sensitive

by altering the permeability properties, but it will also, and quite separately, bind with the chemicals and eliminate them from the system. When there is a low concentration of polysorbate the binding phenomenon is slight, as compared to the sensitization of the cells. As one increases the polysorbate concentration, the cells are still made sensitive but the binding is such that there is virtually no chemical present to be harmful. In support of this hypothesis we have grown cells in nutrient broth, harvested them, washed them, and effectively removed the broth that was there, apart from any trace that might be adsorbed on the cell surface. We have also grown the cells in the presence of polysorbate 80. They were washed in each case. The washing may or may not remove any adsorbed layer on the cells, but it will certainly remove the bulk of the polysorbate. If the cells are then tested with chemicals, the cells that have grown in the presence of polysorbate are significantly more sensitive to chemical attack than the cells grown in its absence.

J. Soc. Cosmetic Chemists **17** 197-211 (1966)

Particle size analysis using Coulter Counters

W. M. WOOD and R. W. LINES*

Presented at the Symposium on "Physical Methods," organised by the Society of Cosmetic Chemists of Great Britain, in Bristol on 16th November 1965.

Synopsis—A relatively new instrument for the size analysis of most forms of particulate material is described. The instrument senses particles suspended in an electrolyte by their momentary displacement of electrolyte, causing an increase of resistance to applied current, as each passes through a small hole, or orifice, in an insulator. Passage is essentially singly, although corrections can be applied for any coincidence loss. Counts at up to 5,000 particles per second are possible, and the resulting size distribution is built up in some twenty minutes, including calculation time, although this can be reduced on a routine basis.

A technique for the size analysis of wide range powders, i.e. those wider than the range of resolution of any particular orifice, is discussed.

The range of new models available working on this same basic principle is reviewed. These reduce calculation time considerably, as well as incorporating many other refinements.

A series of particle size distribution on a wide range of cosmetic materials illustrate the usefulness and versatility of the instrument.

The realization that the size distribution of powders, and other particulate material, is of critical importance to the final product of that material has been achieved in every industry using powders. Particle size affects such things as the definition obtained from phosphors used to coat television tubes, the workability of a metal alloy, the grittiness of food products, the colour of pigments, the solubility and efficiency of pharmaceutical preparations, and the response of control systems in modern high speed aircraft.

No less important are the particles in the cosmetics industry. Simple

* Coulter Electronics Ltd., Dunstable, Beds.

powder formulations such as face powder, talc and rouge depend for their efficiency on the fineness of the powder. Being too fine, however, means a possible health hazard from inhalation.

Colour in lotion is a function of particle size and a colour can be made to appear to have two different shades by a change in particle size. Liquids such as perfumes, colognes and toilet waters must be filtered efficiently not only for their good appearance, but also for health reasons since poorly filtered products can contain substances harmful to the skin.

The earliest form of size analysis equipment was the sieve, followed by the microscope, the sedimentation techniques, and many other methods. All of these methods have their good points but in the main it is fair to say that they are not suited to the demands of a modern industry, which requires an automatic method which is independent of operator error, and which measures each particle individually and accurately.

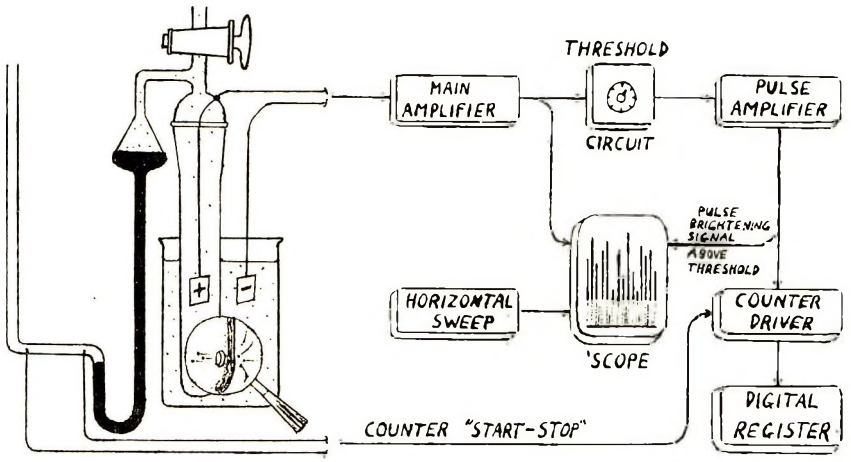

Figure 1 Diagram of Coulter Counter principle

Coulter (1) in 1956 described an instrument for the automatic counting and sizing of blood cells. It has since been shown that the same principle can be applied to a wide range of other particulate materials, with equal speed and accuracy. The size range covered by the instrument is approximately 0.5μ–400μ and the only limitation is that the sample to be analysed must be suspended in an electrically conductive liquid. A stirring system can be employed to avoid settling effects during the size analysis.

A diagram of the instrument is shown in *Fig. 1*. The sample to be

analysed is suspended in a suitable electrolyte in a beaker and placed on the beaker platform. A glass orifice tube, having an accurately made aperture in the lower end projects into the beaker, the inside of the tube being filled with the same electrolyte as in the beaker. On either side of the orifice is an immersed electrode. By applying a controlled vacuum to the orifice and the mercury manometer situated behind it, liquid and the suspended particles are drawn through the aperture. The passage of the particle through the orifice causes a momentary increase in the resistance to the current which is simultaneously passing through the orifice. This increase is detected as a voltage pulse, proportional to the volume of the particle. This pulse is then amplified, scaled, passed through an adjustable threshold and counted, if it exceeds that threshold level, when desired.

Closing the top tap on the control piece cuts off the vacuum and the returning mercury column continues sample flow through the orifice. Set in the manometer are a series of electrodes which enable one to obtain a particle count in varying sample volumes (0.05, 0.5 and 2 ml). A single count above any given size can be made in some 15 sec, and by a repetition of this process a size distribution can be made over as many points as may be necessary in a very short time.

Since the Coulter Counter measures the volume of the particles directly, conversion of particles to volume per cent or for particles of uniform density weight per cent, presents few calculation problems. An example of a typical data sheet is shown in *Fig. 2.*

With the Coulter Counter one of the essential features is the quality of the dispersion, which is, of course, common to all other sizing methods using a suspension. The Counter will count and size anything that is presented to the orifice, so it is vital that one decides whether one requires the size of the particles in the powder or liquid as they are in the original sample, or the size of the discreet particles, and accordingly select the appropriate method of dispersion.

Many methods are available for this purpose, but the one which is currently finding favour is the use of ultrasonics. Small laboratory baths are now commercially available into which are placed the beaker, the sample together with the electrolyte plus some other dispersant, if needed. The time interval needed to obtain a reproducible dispersion is usually between 15 sec and 2 min, according to the ease or difficulty of dispersion. An example of the reproducibility of the method of dispersion, sampling and the Counter is shown in *Table I:*

COULTER COUNTER DATA AND WEIGHT CONVERSION

Sample MEDICATED TOOTHPASTE Source Electrolyte METHANOL + 5% w/v LiCl

Aperture Diameter 50 μ Manometer Volume 0·05 ml Coincidence Factor (P) = 3·125 Calibration Factor (k) = 4·30 Dispersant ULTRASONIC Operator

Aperture Resistance 21 kΩ Calibration and Zero Data Notes Date

Gain Index	t′	I	F	n′ (raw counts)			$\bar{n}'$	$n'' = P\left(\frac{\bar{n}'}{1000}\right)^2$	−✓	$n = \bar{n}' + n''$	$t = t'(F)$	$d = k\sqrt[3]{t}$	Δn	$\bar{t}$	$(\Delta n)\bar{t}$	PROGRESS $\Sigma(\Delta n)\bar{t}$	CUM. WEIGHT %
1	100	1	2·00	3,4,	4,2,	3,2	3·0		1	2·0	200	25·2	2	300	600	600	2·1
3	100	1	1·00	12,14	12,10		12·0		1	11·0	100	20·0	9	150	1350	1950	6·8
"	70	1	"	64,61	58,55		59·5		1	58·5	70	17·7	47·5	85	4037	5987	21·0
"	50	1	"	113	93		103·0		1	102·0	50	15·8	43·5	60	2610	8597	30·2
"	30	1	"	132	139		135·5		2	133·5	30	13·4	21·5	40	1260	9857	34·6
"	20	1	"	228	205		216·5		2	214·5	20	11·7	81	25	2025	11882	41·7
"	"	2	·501	392	417		405		2	403	10·02	9·28	188·5	15·01	2829	14,110	49·5
"	"	3	·252	662	668		665		3	662	5·04	7·36	259	7·53	1950	16,060	56·4
"	"	4	·1269	1196	1195		1169	4	6	1167	2·54	5·87	505	3·79	1916	17,976	63·1
"	"	5	·0675	2025	2071		2018	13	12	2017	1·29	4·69	849	1·915	1627	19,603	68·8
"	"	6	·0339	3792	4052		3922	48	16	3954	·668	3·76	1937	·979	1896	21,499	75·4
"	"	7	·01783	8568	8642		8605	231	29	8807	·357	3·06	4853	·512	2487	23,986	84·2
"	"	8	·01011	17,105	16,879		16,962	897	49	17,810	·202	2·53	9003	·279	2516	26,502	93·0
"	"	9	·00625	26,203	25,218		25,710	2063	82	26,971	·127	2·16	9160	·164	1507	28,009	98·3
4	"	9	·00499	27,801	29,203		28,502	2534	139	30,897	·0898	1·93	3926	·108	426	28,435	99·8
														ASSUME		28,500	100%

Figure 2 Typical data sheet

Table I
Reproduced results on a sample of powder

Particle diameter μ	Cumulative weight % above stated size		
	Run 1	Run 2	Run 3
35	1.1	1.4	1.7
25	9.8	10.4	10.7
20	23.8	26.9	29.5
15	48.0	50.1	52.0
10	78.3	80.1	80.5
7	91.2	93.1	93.4
5	96.8	98.0	98.1
3	99.4	99.6	99.7
2	99.75	99.83	99.93

This was a medium-priced powder and the electrolyte used was 5% trisodium phosphate, and the time in the ultrasonic bath was 20 sec. From *Table I* it will be seen that the reproducibility is within some 3 or 4% on a weight basis at the most sensitive part of the distribution.

Once the sample is dispersed it is essential that no flocculation of the particles occurs, as the Counter will accurately count and size any particle presented to the orifice. In order that this can be prevented it is usual to add some dispersant, preferably a nonionic such as *Nonidet P.42* to the dispersed sample, whilst one can also mechanically stir the suspension during the analysis. This fact enables one to study the stability of emulsions, solubility rates and the effect of dispersants, flocculants, etc., with an ease which has previously been unobtainable.

The choice of the electrolyte is also of considerable importance, the selection being dependent upon the nature of the material under investigation. One does not therefore select a solution which would either dissolve or flocculate the material under test.

Wherever possible a sodium polyphosphate solution, such as *Calgon,* is used as this is itself a dispersant at a concentration of 2–4% by wt. such as can be used on the Counter itself. This type of electrolyte is ideal for the majority of insoluble powders such as talc and rouge. For emulsions of the o/w type sodium chloride at 1% by weight can be used. If the material is water soluble then it is possible to use a non-aqueous electrolyte. A material of this type is calcium carbonate, the electrolyte used being 5% lithium chloride in methanol.

Fig. 3 shows the results obtained on a series of typical toothpastes, the electrolyte in question being the one for calcium carbonate. The slight solubility of the material under test is counteracted by prior saturation in the electrolyte.

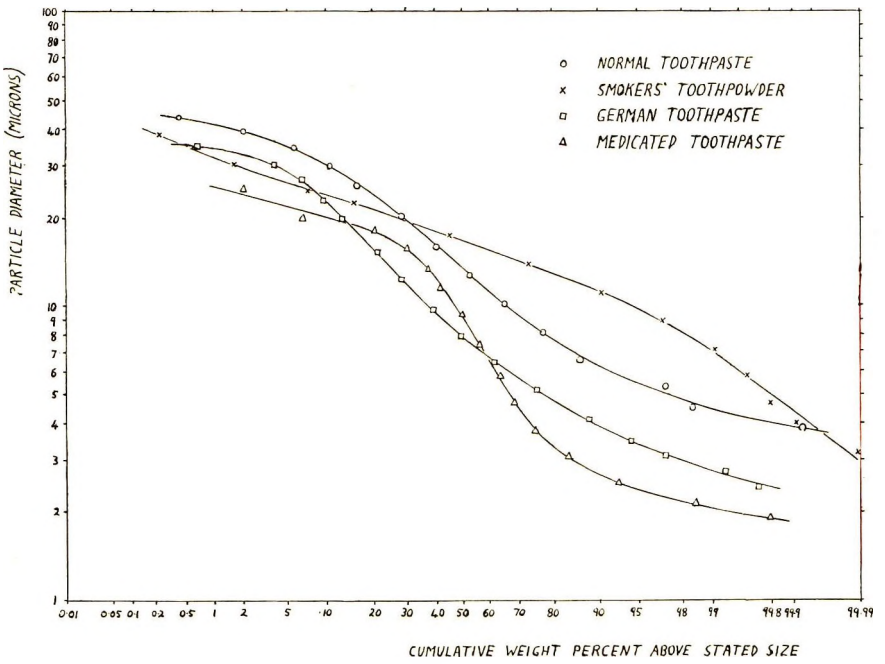

Figure 3 Particle size distributions of typical toothpastes and powders (Logarithmic—probability plot)

The response of the Coulter Counter is relatively independent of particle shape, in that the true volume is always measured over the size range covered by each orifice.

It has been shown that the change in aperture resistance caused by a particle passing through the orifice is:

$$\Delta R = \frac{Po.V}{A^2}\left\{\frac{1}{\frac{1}{1-\frac{Po}{P}}-\frac{a}{XA}}\right\}$$

Where: Po = electrolyte resistivity
A = aperture area normal to axis
V,P,a = particle volume, effective resistivity and area normal to aperture axis
X = particle dimension ratio =

$$l/d = \frac{\text{length along aperture axis}}{\text{diameter of equivalent sphere}}$$

Thus for any given electrical condition and aperture size, response is essentially linear with particle volume, giving insignificant error (1%, on a volume basis) provided that the maximum size measured by any one orifice tube is below 40–50% of its physical diameter.

Particle resistivity has also been proved to have no significant effect on instrument responses. All powders, once they are in suspension behave as non-conductors, this being attributed to either an oxide film on the particle surface or the Helmholtz Double Electrical layer, surrounding each particle. It can also be seen from the above equation that particle density cannot affect response. However, data reduction from volume to weight per cent cannot be made in the case of a mixed powder of varying densities unless the ratio of densities is known and can be attributed at each particle diameter. Temperature change mainly affects the response by the change in electrolyte resistivity. Under normal working conditions this is negligible but a simple correction can be made if necessary.

Particle concentration used in the Coulter Counter is that which gives a maximum number count below the limit of coincidence effects for the orifice tube in use. In terms of sample amount used this is usually of the order of 20–30 mg in 150 ml of electrolyte.

As the method involves the counting of particles suspended in a liquid it is obvious that for any desired accuracy the particulate counts must be significantly higher than that of the base electrolyte. Ideally this solution should be completely particle free but this is a practical impossibility.

In practice, filtration is carried out with cellulose acetate membranes of the Millipore type, and these are satisfactory for aqueous solutions, but for non-aqueous media a glass fibre paper must be used. This, of course, must be supported on a glass sinter to prevent fibres from the paper getting into the electrolyte. Calibration of the Coulter Counter is usually made directly against particles of a known size such as polystyrene latices, spores and pollens, all of which have a fairly low standard deviation about their mean.

As particle volume is measured directly by the instrument settings (threshold dial (t^1) and aperture current switch (I)) then the calculation of particle diameter d, is equal to $K \times 3\sqrt{\text{instrument settings}}$, K being the calibration constant for that aperture tube and electrolyte system.

Since the instrument produces number versus size it can be used for the on-stream control of solutions such as eau-de-colognes. A typical set of results are shown in *Table II*.

Table II
Particle count obtained on various toilet waters

Particle diameter μ	No. of particles per 100 ml of solution		
	Eau de cologne	Lavender water	Perfume
15	1,500	0	20,000
10	9,800	80	113,500
8	11,300	1,000	233,300
6	11,500	1,800	450,000
4	88,000	19,400	1,230,000
2	270,000	355,000	9,000,000
1	60,000,000	5,000,000	—

The smaller the size the more particles were present. In the case of the perfume we were unable to count the vast numbers present at 1μ.

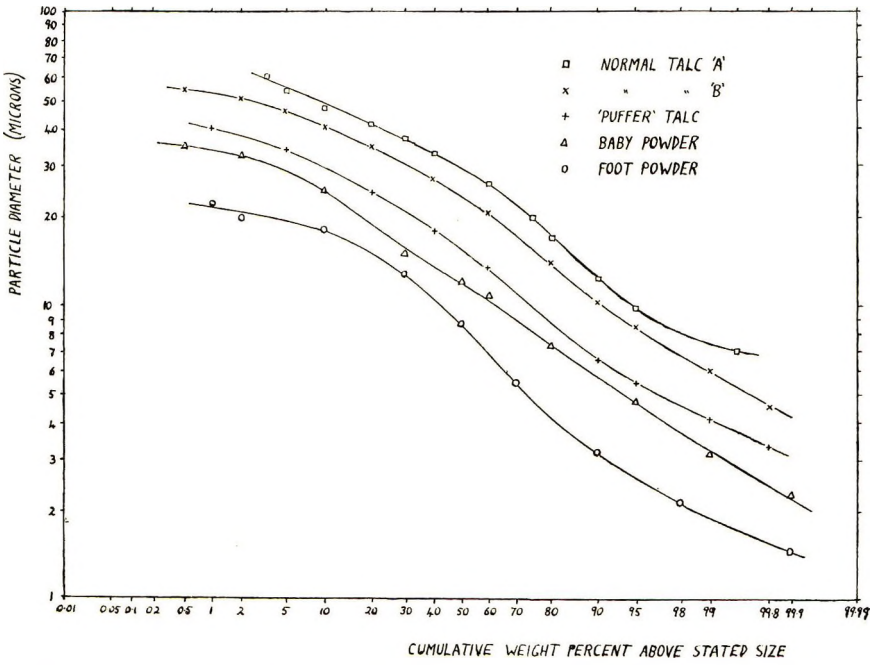

Figure 4 Particle size distributions of various talcs (Logarithmic—probability plot)

Talcum Powders

The particle size of all talc is usually less than 300 mesh (53μ). In particular most baby powders are usually less than 325 mesh (44μ). The optimum range is 10–60μ. *Fig. 4* shows the results obtained with the Coulter Counter on various grades of talcum powder.

It will be seen that they range in size from 65μ down to 1.5μ with a wide range of mean sizes.

A	30.0μ
B	24.6μ
C	15.8μ
D	12.2μ
E	8.7μ

The baby powder is sample D and the range covered is 36–2μ with a mean size of 12.2μ. This would appear to be somewhere within the specification. The electrolyte and dispersion was similar to those previously mentioned.

With some materials the size range lies beyond that covered by one orifice tube, the range of one tube being approximately 1½ or 2–40% of its stated diameter. Clearly when the particle counts are low this upper limit can be extended to 50% or so since the statistical error ($\pm \sqrt{n}$) outweighs the lack of accuracy of response of the sizing circuit. It is possible that some materials have more than 5–10% by weight outside this range on the most suitable aperture. Below this level extrapolation techniques can be used with some degree of accuracy. Extrapolation techniques, however, usually assume that the sample in question follows a log-normal distribution with no second peaks or other variations from normal. This assumption is usually quite correct, but there will be times when an analysis has to be made of the entire size range. Several techniques for this type of analysis exist whereby one combines two or more orifice tubes to cover the range. Basically the techniques are analogous to a microscope analysis – a large field is scanned under low magnification followed by a smaller field under high power, and the distribution built up.

The standard method is as follows: A suspension of the material under test is made up as usual and analysed on a tube suitable for the largest particles present. When the lower limits have been reached, the remaining sample is removed and a smaller tube fitted to the Counter. The suspension is sieved or allowed to settle in order to remove the oversize particles, which would tend to block the smaller tube. Sieving is best accomplished with electro-formed micro-mesh sieves, and these are most efficient when used to wet-sieve dilute suspensions of the type used on the Coulter Counter. The analysis is then continued, overlapping the last few points of the larger tube down to the end of the particle system or until the lower limit of the smaller tube is reached.

It can be argued that whatever method of removing the large particles

from the system is employed some smaller ones will also be removed. In practice, however, the error is insignificant usually being less than 2% in terms of number, and decreasing, which is negligible on a number or weight basis. The calculation then proceeds as normal.

The time taken for a typical single tube analysis including the calculation is 20 min. Two tubes require perhaps another 5–10 min. Times can normally be halved on a routine basis.

Figs. 5 and *6* show the size analysis of various other cosmetic materials obtained with the Coulter Counter.

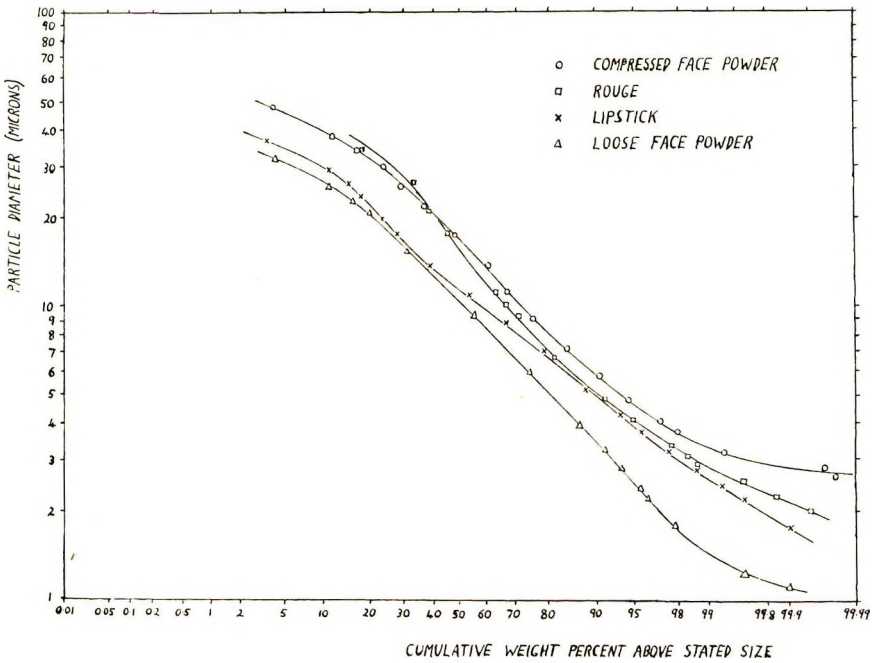

Figure 5 Particle size distributions of various cosmetic materials

The Coulter Counter being already partly automatic is ideally suited to further automation. New Models B and C now lend themselves to this system.

The Model B has two counting circuits so that a frequency number distribution can be obtained directly. Among the many other advantages is that the Model B response is independent of electrolyte resistance so that one calibration factor will hold for changes in electrolyte resistivity caused by concentration change or temperature increase. It also lends itself to easier and faster data reduction. Using a Model J plotter coupled

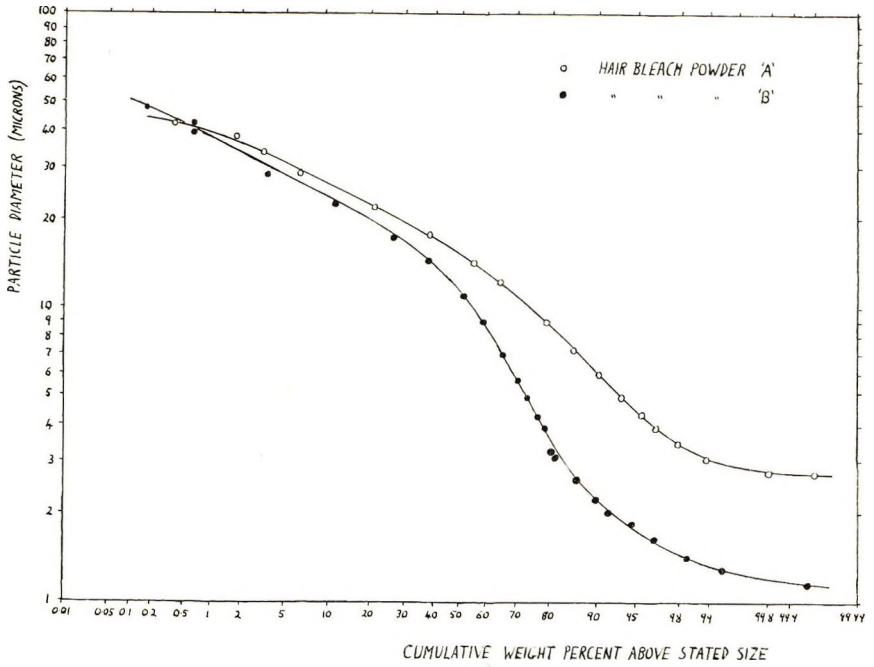

Figure 6 Particle size distributions of various cosmetic materials

to the B Model a frequency or cumulative number histogram can be automatically obtained in 110 sec over 25 points with no operator attention. Each plot is only over a relatively narrow range, about 3-1 on a diameter basis, a wide range distribution can be built up if necessary by the production of several such plots.

A further development is to use the information obtained by the above system, and by coupling the numbers and particle volume, automatically and instantly compile the cumulative volume or weight distribution. This is achieved with the Model M.

The Coulter Counter Model C is the most elaborate model yet commercially available. By utilizing advanced circuitry it is possible to obtain complete a six, nine or twelve point size distribution in as little as 15 sec. Recording of the data can be done in many ways, e.g. simple digital print-out and direct connection to a computor. The model has many other advantages over the original Model A.

Correlation of the Coulter Counter to other methods of particle size analysis has been well studied. This presents no problems if one appreciates the limitations of the various techniques. For instance gravitational

sedimentation cannot generally be relied upon below some 4–5μ when such effects as Brownian movement of the particles by convection currents (even in thermostatically controlled baths) and the actual method of following the analysis all help to reduce the limit one can reach.

We hope that this paper has made clear how this instrument can be used for the size analysis of the majority of cosmetic materials from liquids, creams and emulsions to pastes and powders.

(Received: 1st September 1965)

REFERENCE

(1) Coulter, W. H. Paper presented before the National Electronics Conference, Chicago, Ill., U.S.A. (3rd October 1956).

DISCUSSION

MR. A. MOËS: When one has hydrophobic particles suspended in an electrolyte the quality of the dispersion is not good because of flocculation of the particles. The addition of a nonionic wetting agent such as polysorbate 80 decreases the surface tension and facilitates the dispersion. Do you think that the use of such a wetting agent modifies the di-electric constant of the electrically conductive liquid?

MR. R. W. LINES: The addition of a wetting agent in no way affects the response of the Coulter Counter to particles. Since most materials, whatever their nature, need to be analysed in a fully dispersed state it is necessary to add wetting agent to get the ultimate particle size. The only effect that such addition might have is that a very high concentration might increase the aperture resistance and therefore the calibration constant would change for Model 'A'. This can be overcome by simply finding the calibration constant with your system, including wetting agent.

A problem might arise with a wetting agent of the polysorbate type. Some of these surfactants are not completely water-soluble, and are in a very, very fine colloidal state; in that event a very, very high background of particles would be obtained so that the sensitivity of the size distribution is lost.

MR. A. MOËS: May one use a solution of ionic dispersant directly as an electrically conductive liquid in which to suspend the particles to be analysed?

MR. R. W. LINES: One may use such surfactants directly, but in practice their conductivity in an aqueous medium would be so low in terms of the conductivity needed for the Coulter Counter Model 'A' that the size distribution might suffer at the fine end. It might well be that if a low concentration of such a surfactant were used, one could get to perhaps 5μ, possibly 2-3μ, but one certainly could not get to the very small sizes that probably interest you.

MR. A. MOËS: Since particle concentration is a critical point when the Counter is used, how is it possible to dilute liquid o/w emulsions without giving rise to the coalescence of dispersed droplets?

MR. R. W. LINES: One has to dilute carefully, and a slightly different technique must be employed, depending on the system. Probably the most satisfactory way is to make a two stage dilution, one stage into the de-ionized water, and the second

stage into the salt solution, to which the wetting agent has been added previously. This technique has been described by Marshall and Taylor (2). Their emulsion system was 50% liquid paraffin in water, with 2% w/v methyl cellulose 20 as emulgent. They diluted 1 ml emulsion taken from a mixed suspension with filtered de-ionized water to 100 ml. They then took 0.4 ml of this and diluted it to 100 ml with filtered 0.9% NaCl. They commented that the results were strongly comparable to those from the microscope, within the limits obtainable from both techniques. To quote "the dilution techniques used induced no detectable change in the particle size distribution." A similar conclusion has recently been published by Rowe (3).

MR. A. MOËS: If w/o emulsions have to be tested, what kind of liquid must one to dilute them?

MR. R. W. LINES: According to our knowledge w/o emulsions have not yet been analysed satisfactorily with a Coulter Counter. As one must mix the sample into a liquid which conducts electricity, this liquid must be a solvent to take the oil phase. At the same time, its dielectric constant must be reasonably high to get some salt into it for use with the Counter, and a high dielectric constant means that it is also going to take up water. There are two possibilities that could be tried. One must try to coat the water droplets with something that will not go into the solvent electrolyte. Alternatively, one might freeze the system and measure the size distribution of the ice crystals which will be the same particle size to the Coulter Counter.

MR. A. MOËS: What is the best way to use the threshold circuit when an unknown sample has to be tested?

MR. R. W. LINES: *Fig. 1* indicates that the size distribution on the Coulter Counter appears on a screen as a series of vertical pulses, the height of each pulse being the size of the particle going through the orifice at that instant. Apart from one or two rather minor functions it is the purpose of this screen to indicate the approximate size distribution. In this way one can adjust the sizing controls, the threshold dial and the aperture current switch, in a way that enables one to build up a size distribution over the required range.

MR. T. A. BROCK: In *Table II*, figures are quoted for particle size measurements on colognes and a perfume, and presumably the products were mixed with an electrolyte before measurement. If so which one, and was the resultant mixture clear or cloudy due to the perfume oils being thrown out of solution?

MR. W. M. WOOD: The electrolyte used was 1% NaCl and we were very careful to ensure that the solution was clear; the presence of a cloudy solution would indicate that something peculiar had happened with the electrolyte system, e.g. precipitation. To the best of our knowledge we were counting only the particles present in the cologne.

MR. R. W. LINES: One of the chief advantages of the Coulter Counter is that if one is in any doubt as to whether the distribution that is being counted is the

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(2) Marshall, K. and Taylor, J. Coulter Counter users' meeting, Nottingham, 30/9/1965.
(3) Rowe, E. L., *J. Pharm. Sci.* **54** 260 (1965).

proper one, or whether it is changing, one can always go back over points previously counted. One can see by a change in counts at various size levels, whether anything such as aggregation, flocculation, etc., is occurring.

MR. T. A. BROCK: In *Fig. 5* a distribution is shown for particles present in a lipstick. What do you consider that you were measuring, as presumably the system presented to the Counter was a suspension of the pigments present in an artificial emulsion of the base in the electrolyte?

MR. W. M. WOOD: As the electrolyte system was lithium chloride in methanol we have assumed that this would probably dissolve the lipstick base, and that we were actually counting the pigment dispersion.

DR. M. R. W. BROWN: Is it not true that a particle passes between the electrodes, displaces an equal volume of the electrolyte solution, which causes a change in the electrical properties of the system, in this case the resistance, and this is recorded?

MR. W. M. WOOD: That is so.

DR. M. R. W. BROWN: Every deduction which you make from your measurements therefore depends upon the premise that a particle is displacing an equal volume of an electrolyte, and that an inert particle is displacing an equal volume of an electrolyte solution. Do you have any experience of the electrolyte solution being displaced by something which is not inert, such as a cell coated with a chemical which is intended to kill it, and give it a charge?

MR. W. M. WOOD: The response of the Coulter Counter is in no way affected by the particles going through the orifice. It does not matter whether it is a biological cell or a ceramic particle. The charges on the particle itself, or the resistance of the particle, in no way affects the response of the instrument because one is measuring a volume displacement. The U.S. National Bureau of Standards claim that once particles go into the suspension they form a very thin electron shield or oxide film around them, which is perhaps only 1–2Å thick, and this renders the particle relatively inert within a chosen electrolyte system. Biological material in no way affects the count, and it is possible to size blood cells, bacteria, the larger viruses, etc., without getting a wrong answer due to this charge on the particle itself.

MR. G. PROUT: In our laboratories, the Coulter Counter has been used to count tissue culture cells and bacteria.

The bacteria used were a *Leuconostoc* species approximately 0.8μ by 0.5μ, often in chains up to 4 or 8 cells long. As no satisfactory method could be found to separate these cells into single units the suspensions were counted without any attempt to achieve separation except stirring, using the stirrer attached to the Coulter Counter. The electrolyte used was 0.9% sodium chloride dissolved in nutrient broth and this medium was used to culture the organism. Treating the bacterial population with 1.0% phenol or tannic acid solution in order to affect surface potential, did not affect the reproducibility of the count.

The bacteria were also counted using serial dilution and plating out to give a viable count, and by hemocytometer after dilution and subsequent staining by Gram's method, giving a total count of viable and dead cells.

Invariably the viable count was slightly lower (about 10%) than the hemocyto-

meter count. The hemocytometer count varied between 97% and 101.8% of the Coulter Count.

Sample Results

Tube	50μ
Aperture resistance	21.1 KΩ
Electrolyte	0.9% NaCl in nutrient broth
Coincidence factor	3.125
Manometer volume	0.5 ml
Gain index	3
Calibration factor	2.42
Count per ml	60.4×10^6 organisms per ml

			% of Coulter Count
Hemocytometer count	(i)	61×10^6 organisms per ml	101.0
	(ii)	59.7×10^6 ,, ,, ,,	
	(iii)	61.5×10^6 ,, ,, ,,	
Viable count		56.4×10^6 ,, ,, ,,	93.4

Many references are available, mainly from the U.S.A., of using the Coulter Counter for biological particles, and in several of these correlation has been shown between Coulter results and other counting techniques.

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Rheological studies of new cream bases with the Brookfield Synchro-Lectric viscometer

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

Synopsis—The Fryklöf method for studying plastic systems, using the Brookfield Synchro-Lectric viscometer with T-shaped spindles, is reported. Rheological studies of o/w creams show the suitability of the instrument and the Fryklöf method for plastic systems, e.g. pharmaceutical and cosmetic ointments and creams. Rheograms were constructed from which the yield value and the plastic viscosity could be calculated and from which, in addition, the occurrence of thixotropy or rheodestruction could be observed.

The rheological properties of pharmaceutical and cosmetic ointments and creams are important product dimensions – to describe them completely is to describe consistency, pourability, penetrating characteristics or the ease with which the product may be handled or used. The interrelation between flow properties and other product dimensions often makes measurement of rheological properties the most sensitive or convenient way for the development of a more or less solid preparation and of detecting changes of the preparation in density and stability. For rheological measurements on plastic systems, e.g. ointments and creams, a cup or capillary, orifice, sonic, or falling weight viscometer will fail to give a complete picture of flow properties and, in many cases, will present erroneous results. The viscosity of a Newtonian liquid is independent of the shearing stress and rate of shear. For studies on such a liquid it is therefore unnecessary to know the exact values of these quantities. After the instrument has been calibrated with a liquid of known viscosity, other Newtonian liquids can be determined relative to this liquid. For non-Newtonian liquids and

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plastic materials, however, the viscosity is not an unambiguous quantity but is, in fact, a function of the rate of shear. In such a case, a figure for the viscosity is without any definite value unless the rate of shear, at which it is measured, is given at the time. Actually the interest here lies in a determination of the flow curve or rheogram of the material which necessitates measurements at several definite shearing stresses or rates of shear. For a more general application of a viscometer it is, therefore, desirable that measurements of shearing stresses can be carried out at different rates of shear and that the results obtained can be expressed in absolute units, i.e. the rate of shear in sec^{-1} and the shearing stress in dyne . cm^{-2}. Only multispeed rotational viscometers can be used for such measurements.

The Brookfield Synchro-Lectric viscometer is probably one of the most commonly used rotational viscometers. A relatively large number of publications provide evidence of its use both for scientific investigations and for industrial plant control. Fryklöf (1) has attempted to provide a mathematical background for correct interpretation of the experimental results obtained with this viscometer. In addition, the author has dedeveloped a method of measurement for plastic materials with this intrument which exploits, in a better manner than the methods recommended by the manufacturer and used in the investigations so far published, the possibilities for obtaining information concerning the rheological properties of the material investigated.

The instrument

The principle of the Brookfield viscometer is quite simple. A synchronous motor drives the spindle, immersed in the test material, at a constant speed. The force required to overcome the resistance of the material to rotation of the spindle is provided by a calibrated beryllium-copper spring, the tension of which is read as a deflection of a pointer over a graduated scale rotating with the spindle. The scale reading is proportional to the resistance to rotation and hence also a function of the consistency since the latter is in its turn a function of this resistance.

Several different models exist which can be grouped into four separate series, namely:

LV series for the measurement of liquids with viscosities up to 2,000,000 cP.

RV series for the measurement of liquids with viscosities up to 8,000,000 cP.

HA series for the measurement of liquids with viscosities up to 16,000,000 cP.

HB series for the measurement of liquids with viscosities up to 64,000,000 cP.

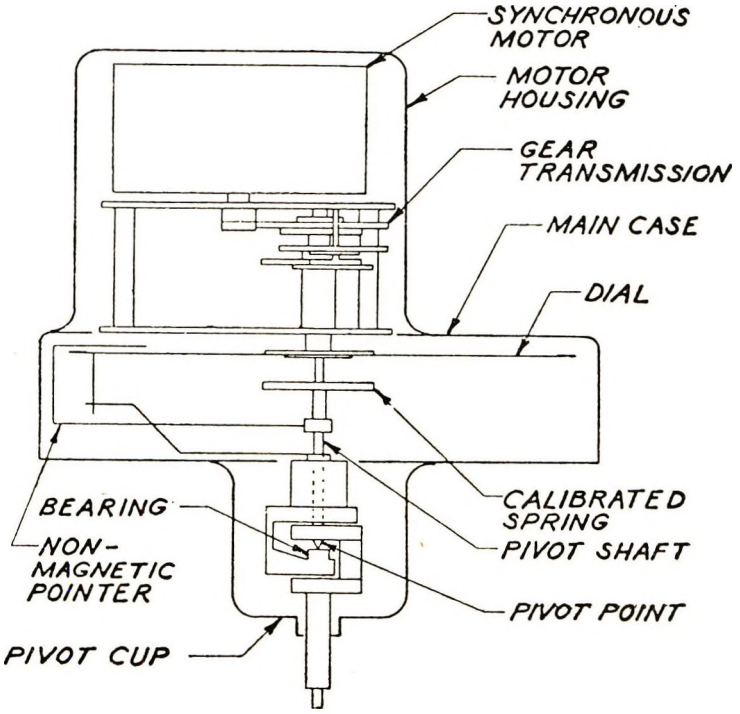

Figure 1
Schematic drawing of the Brookfield Synchro-Lectric viscometer (switches, gear shift, and clutch not shown for the sake of clarity).

To cover different viscosity intervals with sufficient accuracy, each instrument is provided with a number of differently-sized interchangeable spindles, designed for the different ranges of measurements. Moreover, in each series there are models with variable speeds whereby the number of different ranges is further increased. Thus, LVO denotes an instrument with *one* speed in the LV series, LVF an instrument with *four* speeds and LVT an instrument with *eight* speeds. For the LV series, there is also a U.L. adapter, whereby viscosities in the range 0–10 cP can be measured accurately.

To measure the viscosity of liquids, relatively large spindles are used. For the LV instrument, these cylindrical spindles have different heights (hereafter called LV spindles) – the height of the shortest cylinder is,

however, so small that this cylinder is actually disc-shaped. For the other series, the spindles (RV spindles) consist of discs with different diameters. The largest spindle is, however, shaped like a low, hollow inverted cylinder. One spindle in each of the series consists of the spindle shaft alone. For valid calibration of the instrument it is necessary that the measurement should be performed in a vessel of a definite size and that a so-called spindle guard is mounted around the spindle.

For measurements on semi-solid plastic systems, e.g. pharmaceutical ointments, it is necessary to use special, very thin, bar-ty (T-shaped) spindles. These differ from each other only by the length of the cross-piece of the spindle which is responsible for the main part of the torque. The manufacturer recommends that, for these measurements, the instrument should be placed on a "Helipath" stand, i.e. a platform which is lowered continuously throughout the whole of the measurement. This ensures that the spindle will always be moving in a part of the sample which has not previously been subject to mechanical action. By means of the T-shaped spindles, the range of measurement will be extended to

3,330,000 cP for the LV series,
20,000,000 cP for the RV series,
40,000,000 cP for the HA series and
160,000,000 cP for the HB series.

For details concerning the construction of the instrument and its auxiliary equipment, reference can be made to Brookfield's "Instruction manual" and the brochure "Solutions to sticky problems." For our investigations of a new cream base (Ointment Base 601 Witten) with different water contents, we used an RVT model with T-shaped spindles B and E.

As Fryklöf (1) has mentioned, in the instructions accompanying the Brookfield viscometers, there is no information concerning the conversion of the quantities measured experimentally, viz. rotation speed of the spindle and scale reading, to rate of shear and shearing stress. Instead, reference is made to tables in which the scale reading at a certain speed of rotation can be converted to the viscosity in cP. A more serious disadvantage is that in measurements on non-Newtonian substances no comparison is said to be possible between the results obtained with different spindles. As far as such substances are concerned, this limits the use of the apparatus mainly to routine plant control since products with large differences in consistency must necessarily be measured with different spindles.

Fryklöf (1) has shown how to derive equations for the different types

of spindles which make it possible, with certain assumptions, to express the shearing stress and the rate of shear in cgs units. In this way the results obtained with the T-shaped spindles can also be compared independently of the size of the spindle and of the particular viscometer model employed. On the other hand, it has been just as impossible, as with other types of rotational viscometers, to overcome the difficulty that the rheogram for non-Newtonian substances is to a greater or lesser extent influenced by the design of the measuring instrument and the method of using it. The true rate of shear or shearing stress can therefore differ from that calculated according to the formulae given by Fryklöf (1). Since the deviations obtained when using the T-shaped spindles can be relatively large in certain cases, it seems best not to express the results with these spindles in absolute units but instead, in a system of units connected with the apparatus used. These units will, however, be in agreement with the cgs units if the assumptions in the theoretical treatment are fulfilled.

Equations for the T-shaped spindles for plastic systems according to Fryklöf (1)

In measurements on plastic systems which are usually also thixotropic, the large disc-shaped and cylindrical spindles are, as a rule, unsuitable since the immersion of the spindle in the material constitutes a certain mechanical pretreatment. The construction of the T-shaped spindles is, however, such that mechanical pretreatment of this type in the plane of measurement can be avoided which makes these spindles more suitable for thixotropic systems than other types of spindles.

According to Bingham the rate of shear for a uniform plastic is

$$D = \frac{\tau - \tau_f}{U} \qquad \text{(I)}$$

where τ is the shearing stress, τ_f the yield value and U the plastic viscosity. The expression for the torque will therefore consist of one term connected with the yield value and one connected with the plastic flow:

$$M = 6.40 \cdot r \cdot R^{2.08} \tau_f + 87{,}4 \cdot r\, U\, \omega\, R^{2.77} \qquad \text{(II)}$$

$$C = \frac{604}{G} \cdot r \cdot R^{2.08}\, \tau_f + \frac{916}{G} \cdot r\, U\, \Omega\, R^{2.77} \qquad \text{(III)}$$

M is the torque, r the cross-sectional radius of cross-piece of T-shaped spindle, R half the length of cross-piece of T-shaped spindle, C corrected scale reading on the 100 scale, G the spring tension at full scale reading,

ω rotation speed (rad·sec^{-1}) and Ω rotation speed (rpm). The second term in equations (II) and (III) is identical to what applies for Newtonian liquids. For the rate of shear, as in the case of Newtonian liquids, it is

$$D = 3.17 \cdot \Omega \cos \alpha \cdot l^{0.69} \qquad \text{(IV)}$$

α is the angle between the cross-sectional radius and the vertical plane through the cross-piece of the T-shaped spindle, and l the distance from the centre of the spindle.

The corresponding shearing stress is

$$\tau = 0.00346 \cdot \frac{G \cos \alpha \cdot l^{0.69}}{r \cdot R^{2.77}} \cdot \left[C - C_o \left(1 - 0.478 \frac{R^{0.69}}{\cos \alpha \cdot l^{0.69}} \right) \right] \qquad \text{(V)}$$

For those points where $0.478 \dfrac{R^{0.69}}{\cos \alpha \cdot l^{0.69}} = 1$

it is as in the case of Newtonian liquids $\tau = 0.00346 \cdot \dfrac{G \cos \alpha \cdot l^{0.69}}{r \cdot R^{2.77}} \cdot C$ (VI)

At $\Omega = 0$, $C = C_o$ and the shearing stress $\tau =$ the yield value τ_f

$$\tau_f = 0.00166 \cdot \frac{G}{r \cdot R^{2.08}} \cdot C_o \qquad \text{(VII)}$$

The plastic viscosity is obtained from equation (III)

$$U = 0.00109 \cdot \frac{G}{r \, \Omega \, R^{2.77}} \cdot (C - C_o) \qquad \text{(VIII)}$$

As Fryklöf (1) has mentioned, the expressions given involve a certain simplification. They are valid under the assumption that the flow pattern is the same in a plastic system as that in a liquid. In reality, this is not the case for measurements with the T-shaped spindles. When a torque is applied to the spindle, the shearing stress will be greatest at the surface of the spindle and the material will begin to flow within a zone close to the spindle where the shearing stress exceeds the yield value. If the torque is increased, the shear zone will become larger. As the shearing stress at the surface of the spindle increases, the flow pattern will therefore become more and more like that occurring in a liquid. One result of these circumstances is that the values for the rate of shear which are calculated from the rotation speed in the normal way (IV) will be too low in plastic systems or – which is the same thing – the plastic viscosity calculated from (VIII) will be larger than the true value. The deviations will be larger the lower the shearing stress. The rheogram constructed from the experimental values will therefore not be a straight line, as predicted by (I), but rather

a curve which with increasing shear stress should, however, approach more and more the straight line given by (I).

The Bingham flow represents an ideal case. In practice, the flow of a plastic substance is usually non-uniform, i.e. the shear is dependent on time. In such a case the rheogram will no longer be a straight line if the shearing stress is measured at successively increasing rates of shear. By analogy with pseudoplastic liquids, U can often be characterized by an exponential function of the rate of shear $d\gamma/dt$, i.e.

$$U = U_o \cdot \left(\frac{d\gamma}{dt}\right)^{-n} \quad \text{(IX)} \quad U_o = U \text{ at } \frac{d\gamma}{dt} = 0$$

The plastic viscosity therefore varies continually throughout the whole length of the spindle. Hence, when calculating the shearing stress using (V) or (VI), a correction must be introduced. A correction cannot be made in the same way as for pseudoplastic liquids because of the complicated conditions which exist during non-uniform flow, i.e. because the time factor will then be important. For the chosen reference point, it should nevertheless be possible – as for pseudoplastic liquids – to assume that the correction is generally negligible.

In highly thixotropic systems, n can be > 1 at high rates of shear. The true value for τ will then probably differ more from that calculated from (V). In these cases, the calculated values for the shearing stress and plastic viscosity U should be considered to give only the correct order of magnitude. When comparing materials with similar consistency curves, it should be possible as a rule to give the relative ratio of these magnitudes with satisfactory accuracy; this is of importance in the standardization of certain highly thixotropic products, e.g. wool fat and some cream bases. The error due to the curvature of the rheogram for a thixotropic system, and the error due to the fact that the magnitude of the shear zone is dependent on the shearing stress, are of opposite sign. The net error will therefore be less than each of these errors.

Choice of reference point

Using the above equations, it is theoretically possible to determine the shearing stress and rate of shear for any point on the spindle. For the performance of these calculations, the choice of reference point is, however, not a trivial matter. In order to avoid time-consuming calculations of the correction factor in the evaluation of τ in non-Newtonian systems, one should choose a reference point on the spindle such

that the correction can usually be neglected. In plastic systems, τ is directly proportional to C (corrected scale reading on the 100 scale) (V). This results in a considerable complication of the calculation. For those points where

$$0.478 \cdot \frac{R^{0.69}}{\cos\alpha \cdot l^{0.69}} = 1 \qquad (X)$$

this last-mentioned term is zero and the same equation is therefore valid for the calculation of τ in both liquids and plastic systems.

$$\tau = 0.00346 \cdot G \cdot \frac{\cos\alpha \cdot l^{0.69}}{r \cdot R^{2.77}} \cdot C \cdot \left(\frac{R}{l}\right)^{0.69n} \cdot \frac{2.77-0.69n}{2.77} \cdot \frac{1}{(\cos\alpha)^n \int_0^{\pi/2} (\cos\alpha)^{1-n} d\alpha} \qquad (XI)$$

As reference point, one should therefore choose, amongst those points which satisfy the condition in (X), that particular one where the correction factor according to (XI) which was deduced for τ in pseudoplastic liquids exhibits the least average deviation from 1, i.e. that point for which

$$\begin{cases} 0.478 \cdot \dfrac{R^{0.69}}{\cos\alpha \cdot l^{0.69}} = 1 & (X) \\ \displaystyle\int_0^1 \left[\left(\frac{R}{l}\right)^{0.69n} \cdot \frac{2.77-0.69n}{2.77} \cdot \frac{1}{(\cos\alpha)^n \int_0^{\pi/2} (\cos\alpha)^{1-n} d\alpha} - 1 \right]^2 dn = 0 & (XII) \end{cases}$$

The first term written under the integral sign in (XII) is the correction factor just mentioned. Upon solving the system of equations, it is found that this term is a function of n only for those points which satisfy equation (X), i.e. the correction factor is the same for all these points. As stated for pseudoplastic liquids, this correction is generally negligible at these points. Henceforth it is therefore assumed that, for measurements with T-shaped spindles, an arbitrary point satisfying (X) is chosen as reference point. At such a point, for measurements on all materials

$$\frac{d\gamma}{dt} = 1.52 \cdot \Omega R^{0.69} \qquad (XIII)$$

$$\tau = 0.00165 \cdot \frac{G}{r \cdot R^{2.08}} \cdot C \qquad (XIV)$$

Units for T-shaped spindles

It is apparent from the above that the equations given for the T-shaped spindles are based on certain assumptions from which (in certain cases

considerable) deviations can occur when measuring non-Newtonian systems. Values calculated by means of these equations can therefore differ to a certain extent from the true values. It has seemed correct to stress the dependence of these values on the type of apparatus used, by not expressing the results obtained through these equations in cgs units but instead in a special system of units in which the rate of shear is given in B.R.U. (*B*rookfield *r*ate of shear *u*nits) and the shearing stress in B.S.U. (*B*rookfield shearing *s*tress *u*nits) and where, assuming that the equations are completely valid,

$$1 \text{ B.R.U.} = 1 \text{ sec}^{-1} \text{ and}$$

$$1 \text{ B.S.U.} = 1 \text{ dyne} \cdot \text{cm}^{-2}.$$

The viscosity, on the other hand, is given in terms of the cgs unit–poise (P). *Tables I* and *II*, which have been derived from the equations given above, can be used to simplify the calculation of the rate of shear, expressed in B.R.U., and the shear stress, expressed in B.S.U.

Table I

T-shaped spindles. Conversion of rotation speed to rate of shear.

Spindle	Rate of shear (D) in B.R.U. RVT-apparatus Ω, rpm							
	0.5	1	2.5	5	10	20	50	100
A	1.39	2.77	6.93	13.9	27.7	55.4	139	277
B	1.15	2.30	5.75	11.5	23.0	46.0	115	230
C	0.94	1.87	4.67	9.35	18.7	37.4	93.5	187
D	0.78	1.55	3.87	7.75	15.5	31.0	77.5	155
E	0.64	1.27	3.17	6.35	12.7	25.4	63.5	127
F	0.49	0.98	2.45	4.90	9.80	19.6	49.0	98

Table II

T-shaped spindles. Conversion of scale reading to shearing stress.

RV-apparatus, G = 7190: Shearing stress (τ) in B.S.U.

Spindle	Uncorrected scale reading, $S^{1,2}$	Uncorrected scale reading, S_{max}[1]	Corrected scale reading, C
	Each scale division[3] =	Each scale division[3] =	Each scale division[3] =
A	55.4	55.5	55.6
B	97.8	98.1	98.5
C	187	188	190
D	310	316	321
E	546	577	592
F	980	1160	1230

[1] The cross-piece 10 mm below the surface of the test material.
[2] Does not apply to conversion of S_{max} to τ_{max}. Cf the following section of the *Table*.
[3] On the 100 scale.

Measurements on plastic systems

From measurements on a plastic system, it should be possible – provided the range of the rates of shear is not too limited – to construct a rheogram from which the yield value (τ_f) and the plastic viscosity (U) can be calculated. It should also be possible to perform the measurements in such a way that information can be obtained about other matters of interest such as, for example, the existence of thixotropy. An important advantage with the Brookfield viscometer is that measurements can be performed on plastic systems by means of the T-shaped spindles which satisfy the demands stated above and, above all, that the zone of measurement – in contrast to the situation with other types of spindles – is not subjected to mechanical pretreatment when immersing the spindle in the test material. If a spindle is rotated at constant speed in a thixotropic material, the scale reading progressively decreases. This is a sign that the flow is non-uniform and thus gives important information concerning the material.

It seems, however, as though it has been considered a disadvantage that the scale reading does not remain constant during measurements on thixotropic systems. Thus Brookfield's brochure recommends that such measurements should be carried out with a Helipath stand so that the measurement will then always be occurring in a mechanically unpretreated part of the material; thus the scale reading will be independent of the time.

Several points of criticism can be levelled against this method of measurement.

1. The method involves a "one-point" measurement. It is then impossible to characterize a plastic material. Two materials, for which the same result is obtained in a one-point measurement, may have completely different rheological properties. It is often found that one-point measurements are unsuitable even as a means of checking the manufacture of one and the same product.

2. The conditions under which the measurement is performed are not accurately defined. The measurement is *not* carried out in a mechanically unpretreated material. Because the spindle works continuously downwards in a helical path the measurement, in fact, takes place in a material the structure of which is broken down in a significant, though undefined, manner.

3. Constant results are *not* obtained. As the spindle moves down through the material, the torque exerted on the spindle shaft will increase.

In the case of the smallest spindle, e.g. spindle F, the scale reading in a measurement at 1 rpm will be 20% greater after the spindle has made one revolution since it will at the same time have sunk 14 mm further into the material under investigation.

The method suggested here makes use of the possibility of performing the measurements at different rates of shear by varying the speed of rotation. It agrees in its principal features with the methods which are usually used for the recording of rheograms for plastic, thixotropic materials and which have been described, for example, by Green (2).

The measurement of the shearing stress is first performed at progressively increasing rates of shear (up-curve) and thereafter at progressively decreasing rates of shear (down-curve). The possibility of performing measurements of this type is hinted at in Brookfield's brochure "Solutions to sticky problems," but no details are given to indicate how the measurements should be performed or how the results should be interpreted. To use this method, it is necessary to have access to an eight-speed viscometer. Because of its low spring tensions ($G = 674$ dyne · cm), the LVT model can only be used to examine relatively soft creams at a temperature of 20°C. With the RVT ($G = 7190$ dyne · cm) model, measurements can be made on almost all of the existing pharmaceutical and cosmetic ointments and creams, etc. Very firm products, e.g. zinc oxide pastes and wool fat, must be tested on the HBT ($G = 57500$ dyne · cm) model.

The Fryklöf method of measurement

1. The scale must be in such a position that the zero line can only just be seen on the right-hand side of the scale (which rotates from the right to the left). The spindle is immersed so that the crosspiece is 10 mm under the surface of the test material (the shaft of the spindle will then be 16 mm below the surface).

2. The viscometer is started at the lowest speed (0.5 rpm for RV).

3. The largest deflection of the pointer is read off. This is obtained while the spindle is still stationary.

4. The speed is increased to the next speed of measurement. The reading is taken after 60 sec.

5. The measurements are continued, as described under 4, using successively increasing speeds.

6. At the maximum rotation speed, a reading is taken after 60 sec

but this speed is then maintained and further readings are taken after 120 and 180 sec.

7. The speed is decreased to the next lower value. A reading is taken after 15–20 sec.

8. The procedure described under 7 is then repeated at successively decreasing speeds.

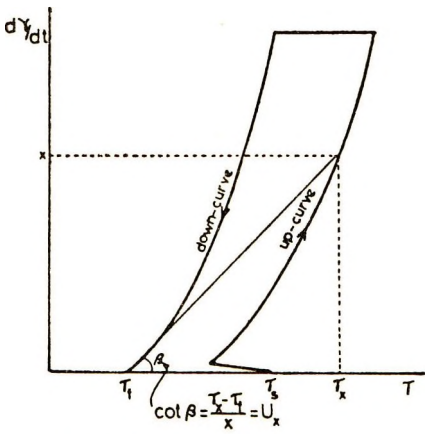

Figure 2 Schematic rheogram.

The following comments apply:—

Stage 3. From the maximum scale reading (S_{max}), the shear stress at $\frac{d\gamma}{dt} = 0$ in the mechanically untreated sample can thus be calculated. That particular value, which is often called the static yield value (τ_s) in the literature and which usually differs from the (theoretical) yield value τ_f calculated from the down-curve of the rheogram (*Fig. 2*), is the largest shear stress that the substance can be subjected to before it begins to flow; it can therefore be said to provide an indication of the structure of the material before shear takes place.

Stages 4–8. The different speeds are unevenly distributed, e.g. for RVT, 0.5, 1, 2.5, 5, 10, 20, 50, 100 rpm. As a rule, the values at closely-adjacent low speeds are of less interest and uncertain, since τ/τ_f is then often small. It is therefore unnecessary to take measurements on the up-curve at 1, 2.5 and 5 rpm (RVT). For the graphical extrapolation of τ_f, on the other hand, it is necessary to include measurements on the down-curve at the lowest speeds. A complete programme of measure-

ments would therefore include measurements at the following speeds (concerning times, etc., see under the respective points 2 – 7), for RVT: 0.5 – 10 – 20 – 50 – 100 – 100 – 100 – 50 – 20 – 10 – 5 – 2.5 – 1 – 0.5 rpm.

Stages 4–5. After 60 sec, the pointer is locked at the particular deflection by depressing the clutch and the speed is immediately altered to the next value in the programme. The operator will then have time to record the scale reading. The clutch must be depressed for the whole time since the spindle would now be rotating at the next speed. After taking the reading, the clutch is released and the pointer will thereafter change to the new value corresponding to that speed.

At the highest speeds [50 and 100 rpm (RVT)], it is not possible to take a reading while the spindle is rotating. Rotation of the spindle must therefore be stopped for a few seconds. No time correction is, however, necessary since a few seconds' difference in the rotation time is negligible after 60 sec.

The reason for the comparatively long time of 60 sec before each reading is taken is due to the fact that the registration of the deflection is not automatic. A few seconds' difference in the time will be of negligible importance, whilst the same error at a rotation time of 15 or 30 sec would result in a considerable uncertainty in the measurement of the up-curve where the break-down of the structure during the first 15–30 sec can be quite rapid.

Stage 6. The readings at the highest rotation speeds are repeated in order that non-uniform flow can be more easily detected.

Stages 7–8. The measurements on the down-curve can be taken at shorter intervals since the values obtained, in contrast to those for the up-curve, are only slightly dependent on the time and thus the reason for the long rotation time is not valid here. It is only necessary to wait until the deflection has become stabilized.

Interpretation of the results

A. A *correction* must be made for the *shaft* of the spindle since the equations given above for the T-shaped spindles are valid only if this has been done. In theory this correction can be obtained by carrying out a complete measurement using only the shaft of the spindle. This, however, means a considerable increase in the amount of work and such measurements with the shaft alone – according to Fryklöf's experience – often give unreliable results in plastic systems. The same

accuracy can be obtained by applying a general, empirically-found correction for all plastic systems, the magnitude of which for different spindles can be found in *Table III*. This procedure is, of course, incorrect from a theoretical point of view since the correction is in reality dependent on the rheological properties of the substance under investigation. Even for strongly thixotropic systems, it has nevertheless been shown that the result obtained in this way differs at most by 5% from the value found when the correction is made using measurements with the spindle shaft alone.

Table III

Correction for the spindle shaft. T-shaped spindles.

Spindle	$C = S$ — correction · S correction[1]	$C_{max} = S_{max}$ — correction · S_{max} correction
A	0.00	0.00
B	0.01	0.00
C	0.02	0.01
D	0.04	0.01
E	0.08	0.02
F	0.20	0.05

[1]Does not apply to correction of S_{max}.

B. A *rheogram* is constructed by plotting, on mm graph paper (*Fig. 3*), the scale reading on the ordinate and the corresponding rotation speed (rpm) on the abscissa. The up-curve is constructed using the values obtained when increasing the rotation speed, and the down-curve similarly when decreasing the speed. The values from 5 rpm to 0.5 rpm on the down-curve are, however, plotted on an auxiliary diagram with a larger scale, in which rpm is used as abscissa, in order to make possible a linear extrapolation of τ_f.

From the diagram thus obtained, it is possible to calculate τ_s, τ_f and U for the reference point mentioned in page 220. τ_s and τ_f are obtained from the values derived from the diagram for S_{max} and S_o by multiplying by a certain factor which has been given in *Table II* for each spindle and which has been calculated from (XIV), after correcting for the influence of the spindle shaft. Since the viscosity usually varies with the rate of shear, the calculation of this property must be made at the same rate of shear, independent of the spindle used for the measurement, if comparable results are to be obtained. For most purposes it is best to calculate the viscosity at 98 B.R.U. (RV, HA and HB with $\Omega_{max} = 100$ rpm)

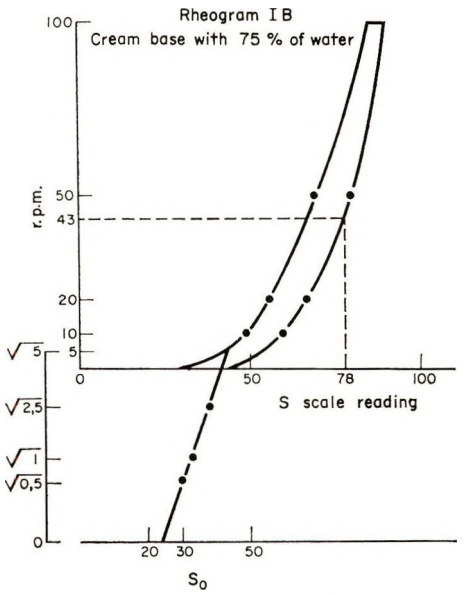

Figure 3

or 58.8 B.R.U. (LV with $\Omega_{max} = 60$ rpm) respectively, which are the largest rates of shear which can be obtained with all the spindles. From *Table IV* it is possible to establish which speed of rotation for the particular spindle corresponds to 98 B.R.U. or 58.8 B.R.U.

Table IV

Spindle	rpm corresponding to	
	$d\gamma/dt$ = 58.8 B.R.U.	$d\gamma/dt$ = 98.0 B.R.U.
A	21	35
B	26	43
C	31	52
D	38	63
E	46	77
F	60	100

The plastic viscosity will then be

$$U = \frac{\tau - \tau_f}{d\gamma/dt} = \text{constant } (S - S_o) \qquad \text{(XV)}$$

The value of the constant is given in *Table V*.

Table V
The constant in equation (XV) for different T-shaped spindles.
Note: (XV) with this constant will give the plastic viscosity in poises (P).

Spindle	LV-apparatus $d\gamma/dt$ = 58.8 B.R.U. G = 674	RV-apparatus $d\gamma/dt$ = 98.0 B.R.U. G = 7190	HA-apparatus $d\gamma/dt$ = 98.0 B.R.U. G = 14370	HB-apparatus $d\gamma/dt$ = 98.0 B.R.U. G = 57500
A	0.0882	0.564	1.13	4.51
B	0.156	0.997	1.99	7.98
C	0.298	1.91	3.82	15.3
D	0.495	3.16	6.32	25.3
E	0.870	5.57	11.1	44.6
F	1.56	10.0	20.0	80.0

The shape of the rheogram, e.g. the curvature of the up-curve and the area between the up- and down-curve, gives an idea of the extent to which the flow is non-uniform, i.e. about thixotropy and rheodestruction. On the basis of values obtained using the Brookfield viscometer, no definite suggestion can, however, be given to show how it is possible to characterize these properties numerically. The relative decrease in the plastic viscosity during the increased rotation time at the highest speed and also the ratio of τ_s and τ_f should, however, indicate the degree of breakdown in the structure due to mechanical treatment.

Experimental

The purpose of this study was to investigate the suitability of the Brookfield viscometer RVT, by using different T-shaped spindles for rheological measurements, on cosmetic cream bases according to the Fryklöf method described. Ointment Base 601 (Chemishe Werke Witten GmbH, Witten, Germany) emulsified with different quantities of water was used. It represents a mixture of partial glycerides of natural vegetable fatty acids with other skin-tolerated, nonionic emulsifiers having the following characteristics:

Acid value	< 1
Saponification value	approx. 100
Iodine value	< 5
Hydroxyl value	approx. 300

Ointment Base 601 is of unctuous consistency so that it can also be used without water, and processed without heating. Emulsification with water is extremely simple. The desired quantity of water is added to the ointment base, which has been liquefied at about 40 to 50°C, either

stirring manually at room temperature or with the aid of a high-speed agitator. Ointment Base 601 is suitable for the preparation of o/w creams.

We prepared three cream bases with 75, 80, and 85% of water, and added 0.1% of a mixture of methyl and propyl esters of *p*hydroxybenzoate as preservative. For the rheological measurements of the different cream bases we used the RVT-model with the T-shaped spindles B and E. As specimen calculations, the experimental values of the measurement of the cream base with 75% of water and spindle B are detailed in *Table VI*. From these a rheogram (*Fig. 3*) is constructed as detailed in page 227. By extrapolating the straight line through the points in the auxiliary diagram, a value for S_o is obtained (= 24). From S_{max}, τ_s is calculated by multiplying by a value (98.1) obtained from *Table II*, section 2 and, from S_o, τ_f is found by multiplying by a value (97.8) obtained from section 1, *Table II*. To calculate the viscosity (U), we first obtained the rotational speed corresponding to $d\gamma/dt$ = 98 B.R.U. (= 43 rpm) from *Table IV*. On the up-curve, S is read off at 43 rpm (= 78). U is then obtained using equation (XV):

$$U = \text{constant} \cdot (S - S_o)$$

where the constant can be found in *Table V*. The calculations are recorded in *Table VI*.

Table VI

Results with 75% water in Ointment Base 601

Apparatus: RVT Spindles: B Temperature: 20.5°C

rpm	scale reading		
	up-curve	down-curve	τ_s = 4414 B.S.U.
	———	S_o 24	τ_f = 2347 B.S.U.
0.5	S_{max} 45	30	U_{98} = 53.8 P
1		33	
2.5		38	
5	↓	43	
10	60	49	
20	67	56	
50	80	69	
100 × 1 min	90	↑	
100 × 2 min	88	|	
100 × 3 min	85	|	

Static yield value (τ_s) = 98.1 × 45 = 4414; τ = shearing stress.
Yield value (τ_f) = 97.8 × 24 = 2347.
Plastic viscosity (U_{98}) = 53.8 P.

Table VII

Experimental values, RVT apparatus, temperature 20.5°C.

rpm	Sample I (75%) Spindle B Scale reading		Sample I (75%) Spindle E Scale reading		Sample II (80%) Spindle B Scale reading		Sample II (80%) Spindle E Scale reading		Sample III (85%) Spindle B Scale reading		Sample III (85%) Spindle E Scale reading	
	up-curve	down-curve	up-curve	down-curve	up-curve	down-curve	up-curve	down-curve	up-curve	down-curve	up-curve	down-curve
	———	$S_0 = 24$	———	$S_0 = 1.9$	———	$S_0 = 11$	———	$S_0 = 2.2$	———	$S_0 = 8$	———	$S_0 = 1.3$
0.5	S_{max} 45	30	S_{max} 6	3	S_{max} 33	15	S_{max} 4.5	2.5	S_{max} 19	11	S_{max} 3	1.5
1	↓	33	↓	3.5	↓	18	↓	3	↓	13	↓	2
2.5	↓	38	↓	4	↓	21	↓	3.5	↓	15	↓	2.3
5	↓	43	↓	5.3	↓	25	↓	3.7	↓	18	↓	2.5
10	6	49	8	6	39	27	6	4.2	25	20	4	3
20	67	56	9	7	42	31	7	5	28	24	4,5	3.5
50	80	69	10	9	49	35	8	6.5	34	30	5	4.5
1 min. 100	90	↑	11.5	↑	55	↑	9	↑	38	↑	6	↑
2 min. 100	88	↑	10.5	↑	51	↑	8.5	↑	32	↑	5.5	↑
3 min. 100	85		10		47		8		31		5	

S_{max} actual maximum scale reading (uncorrected) before the spindle begins to rotate at the lowest rotation speed.
S_0 scale reading (uncorrected) at rotation speed (rpm) = 0.

Results

The results of our rheological measurements presented in *Tables VII* and *VIII* show that the plastic viscosity of the o/w emulsion cream bases decreases with increasing water content. The values of plastic viscosity are independent of the size of the T-shaped spindles used for each sample

Table VIII
Calculated values from rheograms

Sample	Spindle	τ_s	τ_f	U	ratio τ_s/τ_f
I (75%)	B	4414 B.S.U.	2347 B.S.U.	53.8 P	1.88 } 2.6
I (75%)	E	3462 B.S.U.	1037 B.S.U.	50.7 P	3.33 }
II (80%)	B	3334 B.S.U.	1076 B.S.U.	35.9 P	3.10 } 2.7
II (80%)	E	2597 B.S.U.	1157 B.S.U.	35.7 P	2.24 }
III (85%)	B	1864 B.S.U.	782 B.S.U.	24.9 P	2.30 } 2.4
III (85%)	E	1731 B.S.U.	710 B.S.U.	23.9 P	2.44 }

τ_s = static yield value; τ_f = yield value; U = plastic viscosity.
B.S.U. (Brookfield shearing stress units) = 1 dyne · cm^{-2}.
P (Poise); 1 Poise = 1 g · cm^{-1} · sec^{-1}.

within the limits of reproducibility of the method. The experimental values of *Table VII* show that the cream bases investigated are thixotropic. We can confirm the results of Fryklöf that the Brookfield viscometer with T-shaped spindles is suitable for measurements on plastic systems, e.g. pharmaceutical and cosmetic ointments and creams using his suggested method (1).

(*Received: 14th September 1965*)

REFERENCES

(1) Fryklöf, L.-E. *Svensk Farm. Tidskr.* **65**, 753 (1961).
(2) Green, H. *Industrial Rheology and Rheological Structures* 50 (1949) (New York).

DISCUSSION

Mr. P. Sherman: I am a little puzzled at your choice of the Brookfield viscometer because you so rightly point out that the geometry of the spindle is such that it is almost impossible to calculate absolute values of stress or rate of shear. In the method developed by Fryklöf you make the basic assumption that the flow pattern around plastic systems is exactly the same as for liquid systems; this is completely untrue, because in any plastic or pseudoplastic system, apart from treatment at very high rate of shear, you have a flocculation pattern, i.e. the globules are conglomerated to give irregular shaped bodies, and the flow pattern will depend upon the shape of these. This will vary quite naturally as you increase the rate of shear. The initial complex structure gradually deteriorates into smaller, simpler structures and eventually at very high rates of shear you are left with individual globules. Only at

the infinitely high rates of shear would the flow pattern be the same as for Newtonian liquid systems, and I therefore suggest that you would be very much better suited in using the Haake "Rotovisko" coaxial cylinder viscometer. I am a little worried about the interpretation of *Fig. 3*. I know a lot of stress has been placed upon these during the last 20 or 30 years, but it seems to me that one factor is ignored in a study of this type. One first of all increases the rate of shear and measures the viscosity as one goes up the rate of shear scale which is quite acceptable; one then waits a few minutes and starts going down from high to low rate of shear, but at any particular rate of shear there is a time factor involved before the structure can recover, and this is completely ignored in producing histeresis curves. This means that one will get something which is completely untrue if measurements are carried out successively from high to low rate of shear without any interval. I think that it is much more suitable to use a system suggested by Professor Umstedter ca. 1930, i.e. a three-dimensional plot including a time axis.

THE LECTURER: I have found that the reproducibility with the "Rotovisko" viscometer is not so good as with the Brookfield. We have carried out repeated measurements at one-day intervals because it is impossible to repeat these measurements one after another, due to rheodestruction. We have also repeated the measurements after one and two weeks' intervals and have obtained reproducible values. We now have the possibility to predict some properties of creams and to compare these with older preparations. The Helipath stand unfortunately did not give reproducible results, especially for thixotropy, as the spindle at the same point does not allow us to construct rheograms from the values obtained.

MR. P. SHERMAN: I am not surprised that you carried out experiments with the Haake, and were unable to reproduce these one or two days later. If you get correlation at all with the Brookfield I would be inclined to say the Brookfield was in error and not the Haake. We have carried out very close studies at a very wide range of shears, from very high ones down to fractions of a reciprocal second, and find in every emulsion system (we are particularly interested in concentrated w/o emulsions approaching the consistency of those that you have used) that their rheological properties are changing from the moment they are made. We have also found, when working at very low rates of shear, that on measuring viscosity one can get a three or four fold decrease in the value of the viscosity within 40 to 24 hr of manufacture. It is therefore not surprising that you can not get reproducible results with a Haake if you test immediately after preparation, and 24 hr later.

THE LECTURER: Our emulsions were stable, and the flocculation which you have mentioned will appear in unstable emulsions and to a lesser extent in stable emulsions.

MR. P. SHERMAN: In a w/o emulsion you will get flocculation from the moment of preparation. Stability, however, has nothing to do with flocculation; it refers to the coagulation or coalescence of the droplets, and the rheological changes are primarily due to this. You will find that in an emulsion system you have a certain proportion of very small droplets which are very unstable, even though the larger droplets are stable; these very small droplets contribute enormously to the rheological parts of the system. They are very unstable and disappear within one or two days of manufacture.

MR. N. J. VAN ABBÉ: For many years I have been bothered by the discreet

speeds employed in the Brookfield and, for instance, the Epprecht rheomat, where the speed change is by a jerk as it were. In the Ferranti Shirley there is a continuous speed range. I would like your comments on the possible significance of this. It seems to me that the Ferranti Shirley, in particular, makes a very good colloid mill, and the measurement is not on the product that one first started measuring. This appears to point in favour of the Brookfield where, at any rate the surface area of the spindle is not very great. On the other hand, the criticized Helipath device ensures that emulsification is kept to a minimum. Do you not think that this is a point in favour of its use?

THE LECTURER: I think that at the lower speeds of 1 and 0.5 rpm the spindle is revolving so slowly through the material that the torque is much higher a[illegible] low rates of shear, and therefore the measurements are incorrect. There is a varying pressure on the material and you therefore have a side effect which cannot be measured accurately. The instrument must be suitable for measurements of Newtonian and pseudo-plastic fluids but not for plastic thixotropic material.

Book reviews

THE BIOCHEMISTRY OF THE NUCLEIC ACIDS. 5th Edn.

J. N. Davidson. Pp. xv + 352 + Ill. (1965). *Methuen & Co., Ltd., London.* 35s. U.K. only.

The first edition of Professor Davidson's book appeared in 1950. The appearance of this, the fifth edition, after only 15 years is a measure, not only of the popularity of the book, but of the tremendous progress made in the study of the chemistry and functions of nucleic acids over this period. It is, of course, a topic of compelling interest to everyone, and there can be few chemists and biologists who do not wish to be at least acquainted with current developments in the field.

The book is intended to provide an elementary outline of the main features of the nucleic acids and nucleoproteins for the benefit of students of biochemistry, of chemists who wish to know something about the biological aspects of the subject, and of biologists who wish to learn a little about the chemical aspects. It falls naturally into two halves, which may be said to be the static and dynamic aspects of the subject respectively. Commencing with a description of hydrolysis products and chromatographic behaviour, the first half continues with the preparation, structure and properties of RNA and DNA, a discussion of nucleases and related enzymes, and proceeds through chemical methods of estimation and histochemistry to a discussion of nucleic acids in viruses. In the second half are the chapters of more dramatic interest, being a discussion of the biosyntheses of DNA and RNA, and a description of their functional involvement in transfer of genetic information and in protein synthesis. Coverage of the whole field of nucleic acid biochemistry is completed with chapters on biosynthesis and catabolism of the nucleotides.

Professor Davidson states that the book has become known in his laboratory as "The Child's Guide to the Nucleic Acids." This is legitimate comment only in so far as the book is lucidly written and is easily read by the non-specialist. The information contained is nevertheless detailed and comprehensive, and is up to date to January 1965. Each chapter contains a long list of references for further reading, and the book possesses a good index. It is to be thoroughly recommended for anyone wishing an introduction to, or a refresher course on, the subject.

There remains one small point of criticism. The two-page list of abbreviations at the beginning of the book does not include all the abbreviations used in the text, and the occasional searching back through a chapter to find a definition can be a minor irritation. B. G. OVERELL.

INTERPRETATION OF ORGANIC SPECTRA. Editor: D. W. Mathieson. Pp. ix + 179 + Ill. (1965). *Academic Press, London and New York.* 42s.

This is a pragmatic book, intended to give practice in the interpretation of three important fields of diagnostic organic spectrometry. As an editorial principle, the sections are self-contained – up to ten illustrative spectra are discussed in detail but deliberately making reference to little or no ancillary chemical, physical or other spectroscopic data. This unnatural isolation helps to focus attention on both the strength and the weaknesses of nmr, ir and mass spectrometry as diagnostic tools. Moreover the authors assume prior knowledge not only of the principles, which in fact most empirical texts do, but also experimental procedures and to a certain extent terminology. On reflection one must agree that this is fair since it is the newly practising spectroscopist who mainly will wish to use this work. It may be noted that Bellamy (1), which is one of the best known standard texts on the interpretation of ir spectra, adopts a similar embargo; however Scott (2) includes a most useful general introduction on the electronic significance of uv spectroscopic measurements. It is arguable just how much background material an author should include to widen the scope and potential readership but at the same time risk unduly increasing the size (and price) of the book.

The first part is allegedly concerned with nmr but in fact deals entirely with *proton* magnetic resonance spectra – which is what most users will want. The so-called "Introduction" is no exception to the editorial rule, the reader is indulged to the extent that there is a brief and simple example of splitting rules for adjacent proton interaction (in the ethoxy group) but he is then unsettled by being assured that in practice the idealized first order coupling pattern is rarely met. In this respect the introductory discussion in the nmr chapter in Schwarz (3) is to be preferred (but even those explanations are sometimes a little disjointed). The main section comprises a series of ten examples of pmr spectra which are discussed minutely and are fascinating to work through, although the occasional catagoric statement, apparently made *ex cathedra*, is not always rationalizable on closer study. Misprints are few but a mistake in the molecular formula that is given with Example 10 may, temporarily, be most misleading. Judging by the difficulty which your reviewer encountered in seeking to solve the six supplementary unworked examples, a single reading of this book, without reference elsewhere, is not sufficient to acquire proficiency in the interpretation of pmr spectra – but it certainly gives one a very fair initiation into its problems.

With regard to the display of *ir spectra*, inevitably the conflict of different conventions arises. Thus both wavelength and wave-number scales are engraved on every spectrum but some readers will be irritated to find that many of the traces have the absorbance increasing from top to bottom of the charts. All the bands in these spectra are annotated and discussed in reciprocal cm units, but wavelengths can easily be read off from the generally linear upper abscissa. Nevertheless the casual reader must be alert for changes in the scanning speed at certain frequencies. Following the editorial principle, previous acquaintance with the nature of skeletal

(1) Bellamy, L. J. *Infra-red spectra of complex molecules*, 2nd. edn. 1958.
(2) *J.* **16** 480 (1965).
(3) Schwarz, J. C. P., *Physical methods in organic chemistry*, 1964.

vibrational (and rotational) deformations is assumed and the text comprises an empirical discussion of worked examples. Although the spectra are examined in isolation, the author rightly emphasizes the importance of supplementary physical data in narrowing the field of possible structures and that it is the exception rather than the rule to effect a complete structural identification from the ir spectrum alone. The series of examples comprise hydrocarbons of increasing complexity and unsaturation, followed by the introduction of various functional groups; natural extracts as well as specific compounds are considered. Compared with the pmr section, there is rather more discussion in the form of interesting extensions to general cases from the particular examples given. Instead of correlation tables for functional groups in various environments, there is constant reference to Bellamy and to the other well used standard work, Jones and Sandorfy (4).

The section on mass spectroscopy begins with some useful empirical tips for the general examination of low resolution spectra, including the use of isotopic abundance ratios particularly for identifying parent peaks, the stability of various systems reflected in the strength of their parent ions, the unique situation of mass sums for odd numbers of nitrogen atoms and the so-called "z number" classification for codifying the degree of unsaturation of hydrocarbons and – by suitable correction – other functional substitution. Examples are developed from the logical consideration of the cracking patterns of relatively simple molecules, noting particularly the bonds at which cleavage preferentially occurs for different functions and the particular mass ratios favoured thereby, which being independent of chain length are diagnostic for that function. References are given sequentially to authors who have specifically reviewed the various functions and to the American Petroleum Institute collection of mass spectra for the unique allocation of a cracking pattern to a particular hydrocarbon. The impression given is that the interpretation of mass spectra is a notably more intuitive exercise than the consideration of pmr or ir spectra. The use of a computer would seem a considerable advantage in rejecting numerous competing structures, particularly for the polyfunctional compounds of higher molecular weight; reference to such a sophisticated approach for high resolution mass spectroscopy was made when reviewing (5) Biemann's contribution to the 3rd IUPAC symposium on the chemistry of natural products. It should be emphasized, however, that the present book is concerned with low resolution, single focussing instruments; the very expensive double focussing machines are still sufficiently rare not to warrant consideration in a manual of interpretation for the majority of practising organic chemists. There is therefore no distinction between the masses of CH_4, NH_2 or O, except that one may recognize the proportion of carbon atoms from the intensity of the "shadows" due to ^{13}C isotope.

The pmr and ir sections of this book are based upon a practical course presented by the authors at the very successful summer school in spectroscopy organized by the R.I.C. in 1964. The ir section is not by itself usable as a source book but is essentially a tutorial work. The previous section however sets out – and largely succeeds – in doing both for pmr spectra. The account of low resolution mass spectra has been prepared by two well-known practitioners. Altogether Dr. Mathieson has supplied a very stimulating text book for the newly practising spectroscopist.

G. F. PHILLIPS.

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(4) Jones, R. N. & Sandorfy, C. Vol. IX of *Technique of organic chemistry*, (1956).
(5) *J.* **16** 418 (1965).

INORGANIC CHEMISTRY IN NON-AQUEOUS SOLVENTS

A. K. Holliday and A. G. Massey Pp. viii + 143 + Ill. (1965). *Pergamon Press, London.* 17/6.

In their preface the authors state that this book is intended for undergraduate chemistry students, including those at "A" and "S" levels, and for the non-specialist student. It is also suggested as an introductory work for research students who wish to use non-aqueous systems. There is no doubt that the book largely achieves these aims.

There is a general introduction describing solution processes and giving definitions. This is followed by two chapters on liquid ammonia and reactions in liquid ammonia. Methods of manipulation of the solvent are described and reaction mechanisms explored. There is a short section on other anhydrous amines. Protonic solvents, including sulphuric acid, are described in a chapter which also deals with the relative strengths of acids and bases. Two further chapters are devoted to non-protonic solvents and the properties and uses of fused salts as solvents and reaction media.

The book is in all parts readable and avoids catalogues of reactions. Analytical applications of non-aqueous solvents are included as parts of the text and not as a single section. Evidence for structures and mechanisms is well presented and experimental techniques are dealt with in sufficient detail to make this a good bench handbook where non-aqueous and fused salt systems are in use. For those readers requiring more specialized information there is a short list of recommended further reading at the end of each chapter. It is a pity that solvent systems such as hydrogen cyanide, hydrogen sulphide and nitrosyl chloride are not described and the index could have been fuller, but as a general introduction to the subject this paperback has much to recommend it. G. S. INGRAM.

POLYMER TECHNOLOGY.

D. C. Miles and J. H. Briston. Pp. xi + 444 + Ill. (1965). *Chemical Publishing Co., New York.* $12.50.

This is the U.S. edition of an earlier U.K. text-book, originally intended for students seeking the Graduateship of the Plastics Institute, and to which had been added chapters on synthetic natural and modified rubber. The book is written in a simple unaffected style commendable to the student, whilst the self-contained chapters and generally adequate index render information readily accessible to casual consultation. It is well illustrated including 32 photographs and innumerable neat block diagrams; chemical formulae are tidily set and errors are rare.

The "Introduction" includes suitable definitions and discusses in general terms polymerization reactions – distinguishing between addition, copolymerization and condensation mechanisms. There is also a short review of the development of the plastics industry. Raw materials are classified into natural products (including celluloses, proteins and exudates) and those derived from coal and from petroleum. The coverage, although superficial, is adequate and moreover is conveniently tabulated for tutorial purposes. Part II, the major portion of the book, gives detailed attention to thermosetting polymers (phenol and amine derivatives, polyesters, epoxy resins, silicones and polyurethanes), thermoplastics (homo- and copolymers of unsaturated momomers and halogenated functions), natural polymers

and natural, modified and synthetic rubbers. Recent work with inorganic and metallo-organic polymers is briefly reviewed. The function of, and optimum requirements for, structural components such as plasticizers, extenders, stabilizers, chelating agents and antioxidants, are examined and a final chapter considers the choice and effect of fillers, colorants, flame retardants, blowing agents and uv absorbants. In Part III, five groups of techniques are described: For thermosetting plastics – compression and transfer moulding; for thermoplastics – extrusion, injection and blow moulding, thermoforming and miscellaneous processes such as calendering, coating and welding. The final Part begins with a section indicating the variety of available physical – including electrical – test methods, without giving procedural details; this section might well have been expanded. There is then a useful qualitative scheme that summarizes familiar flame, odour and appearance tests, with generally satisfactory chemical confirmatory methods for each type of polymer.

In the past one has generally perforce relied upon specialist monographs or manufacturers' handbooks to keep abreast of developments with new polymers or new production techniques. This book bridges the gap between such publications and cumbersome multi-author compendia. It is not only chemical engineers and plastics technologists who will profit from this comprehensive work – any worker concerned with the industrial application of polymers is likely to find useful guidance whilst the specialist seeking further details is given specific suggestions for advanced reading. G. F. PHILLIPS.

THE CHEMICAL CONSTITUTION OF NATURAL FATS.

T. P. Hilditch and P. N. Williams. 4th edn. Pp. xv + 745 + Ill. (1964). *Chapman & Hall, London.* 150s. (U.K. only).

During the eight years which have elapsed since the publication of the third edition of "Hilditch," spectacular advances have been made in separational analytical techniques, especially gas chromatography, and nowhere has the effect of this been more apparent than in the field of natural oils and fats. The result has been a massive influx of information on chemical constitution necessitating extensive revision and rewriting.

Professor Hilditch was joined in the preparation of the fourth edition by Dr. P. N. Williams. The basic plan of the volume remains the same, the changes being in the balance of the various sections and in the amount of detailed information included, to a large extent in tabular form.

The contents may be best summarized by listing the chapter headings:

I: Introductory survey of natural fats.
II: The component acids of fats of aquatic flora and fauna.
III: The component acids of fats of land animals.
IV: The component acids of vegetable fats.
V: The component glycerides of natural fats: general survey.
VI: The component glycerides of individual vegetable fats.
VII: The component glycerides of individual animal fats.
VIII: Some aspects of the biosynthesis of fats.
IX: Constitution of individual natural fatty acids.
X: Synthetic glycerides: naturally occurring fatty alcohols: acyl ethers of glycerol.

XI: Notes on experimental techniques employed in the quantitative investigation of fats.

The individual sections are supported by comprehensive bibliographies, some of the references being as recent as early 1964. Excellent indexes include a general index of subjects, indexes of individual fats and waxes, plant families, individual fatty acids and individual glycerides.

This first-class volume is absolutely essential for every cosmetics laboratory and will serve as a major reference work on oils and fats for many years to come.

R. P. REEVES.

THE KJELDAHL METHOD FOR ORGANIC NITROGEN.

R. B. Bradstreet. Pp. viii + 239 + Ill. (1965). *Academic Press, New York and London.* 76s.

The Kjeldahl method is an example par excellence of a well-established analytical method of which the theoretical chemistry is rather obscure. The many modifications which have been proposed to the method have consequently tended to be *ad hoc* improvements directed at a particular type of sample. In this monograph, Bradstreet has attempted to draw together the various strands of research, both the relatively few concerned with elucidation of mechanisms and the many with the principal aim of improvement and adaptation of the method. The result is an interesting and readable review.

The eight-page Introduction is a brief history reminding us of the origin of the method in the Carlsberg Laboratories in Denmark and Kjeldahl's first publication in 1883. The 47 references quoted are selected to illustrate the 80 years of its history.

The second chapter entitled "Kjeldahl digestion" discusses, in 81 pages, acid requirements, salt additions, oxidizing agents, boiling time and catalysts. The amounts of acid consumed by various types of sample and the effect of the salt addition in raising the temperature of digestion are critically examined; the advantages of using oxidizing agents prior to the digestion proper are discussed, as are the reducing agents which may be used to enable substances containing nitrogen directly bonded to oxygen to be determined.

The function attributed (p. 61) to salicylic acid in preventing loss of nitrate nitrogen, viz. to supply a source of sulphur dioxide, is quite different to that which many chemists faithfully imbibed from standard texts, where salicylic acid is described as a substance that can be readily nitrated. Unfortunately for such illusions logic appears to be on the author's side. The controversy over catalysts has received due attention concluding with reasons for the general acceptance of mercury nowadays.

The following chapter on digestion procedure overlaps in subject matter with the previous one but this is admitted by the author as a necessary fault, if the form of sub-division of the book is accepted and yet completeness is to be maintained within each part of the discussion. The chapter discusses treatments necessary for natural products from cereals and soils to coal and petroleum, and for organic substances according to function, and ends with eight pages devoted to "sub-micro" methods where the amount of nitrogen is within the range 0–100μg. The reviewer deprecates the use of the symbol λ in this context, particularly as the author has been sufficiently inconsistent as to use the more widely understood μl at least once (p. 134).

The final chapter of 22 pages, deals with methods of determination of ammonia in Kjeldahl digests or in resulting distillates, and comprises a straight-forward review of such methods. The volume ends with 66 pp. of bibliography; from a brief examination this appears to be as comprehensive as would be hoped for such a monograph.

Whilst clearly the larger laboratories, and also smaller ones using the method a great deal, will find such a volume almost a necessity for their libraries, its high price presumably associated with its American origin, will deter many smaller users from purchasing the book. M. J. GLOVER.

1966 DINNER AND DANCE

The President and Mrs. Clark

Dr. Carriere (Guest of Honour)
and the President

Society of Cosmetic Chemists of Great Britain

1966 DINNER AND DANCE

Dr. G. Carriere, D.Sc. (Unilever N.V., Rotterdam), Central Coordinator for Legislation of the International Federation of Societies of Cosmetic Chemists, was the Guest of Honour at the Society's Annual Dinner and Dance. This year it was held at the Europa Hotel, London, where a large number of members and their friends spent an enjoyable evening together.

The toast of the guests was proposed by the President, who mentioned that the Society, although still small and young, was a respected one. He felt that the objects of the Founders—to establish and maintain the status of the cosmetic chemist—were being achieved, and that this was evidenced by the value placed on the Journal, Symposia and the Diploma Course. Mr. Clark was glad to welcome a number of guests including Mr. Seager, representing the T.P.F., and his wife. In introducing Dr. Carriere, Mr. Clark praised his linguistic abilities and his wit as an after-dinner speaker.

Dr. Carriere replied to the toast in a humorous vein, drawing upon his many experiences in Europe and America over a period of two years, during which he had lectured on cosmetic legislation. He emphasized the importance of a combined effort by manufacturers and scientists on committees considering legislation of this nature.

1966 PROGRAMME

LECTURE:

Wednesday, 13th April.

Some aspects of laboratory planning

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

FILM EVENING:

Thursday, 19th May.

Venue: The Royal Society of Arts, John Adam Street, London, W.C.2.
Time: 7.30 p.m.

ANNUAL GENERAL MEETING:

Monday, 23rd May.

Washington Hotel, Curzon Street, London, W.1, at 7 p.m.

SYMPOSIUM ON COLOUR

A Symposium on Colour will be held at the Grand Hotel, Eastbourne, Sussex, on 26th and 27th April 1966. Participation is permitted only when application has been made on the appropriate form, and the fee duly paid. This is £5 5s. for each participant who is a member of one of the Societies of Cosmetic Chemists affiliated to the I.F.S.C.C. The registration fee for non-members is £8 8s. Registration forms giving all details are available from the General Secretary, Mrs. D. Mott, 18 Warner Close, Harlington, Middx.

PROGRAMME

Tuesday, 26th April 1966

Chairman: R. CLARK, ESQ., President

Morning

9.30 "Colour and vision."
DR. F. J. J. CLARKE (*Light Division, N.P.L., Teddington*).

10.15 "Colour measurement."
P. R. BUNKALL (*I.C.I. Dyestuffs Division, Manchester*).

10.45 COFFEE.

11.00 "Instrumental colour matching control."
R. P. BEST (*B.I.P. Chemicals Ltd., Birmingham*).

11.30 "Subjective aspects of colour."
M. DREWITT (*British Colour Council, London*).

12.00 "Colour slides illustrating use of uv absorbers."
R. N. HOWARD (*General Aniline and Film Corporation, New York*).

13.00 SYMPOSIUM LUNCH.

15.30–17.00 Display of apparatus and equipment at School of Pharmacy, Brighton College of Technology, Moulsecoomb, Brighton 7.

20.00 SYMPOSIUM DINNER.

Wednesday, 27th April 1966

Chairman: DR. A. W. MIDDLETON, Vice-President

Morning

9.30 "The toxicology of artificial colouring materials."
L. GOLBERG, M.A., M.B., B.Chir., D.Phil., D.Sc., F.R.I.C., F.C.Path., F.I.Biol. (*B.I.B.R.A., Carshalton*).

10.00 "Reactions to artificial colouring materials."
PROF. C. D. CALNAN, M.A., M.B., B.Ch., F.R.C.P.
(*Institute of Dermatology, London*).

10.30 COFFEE.

10.45 "The inter-relationship between the melanocyte system and keratinization."
A. JARRETT, M.B., Ch.B., F.R.C.P., M.C.Path.
(*University College Hospital Medical School, London*).

11.15 "Measurement of the effect of hair colourants."
B. A. SCOTT, B.Sc., Ph.D., A.R.I.C., and M. W. PARSLOW
(*Unilever Research Laboratory, Isleworth*).

12.00 Civic Reception by the Mayor of Eastbourne at the Winter Garden.

13.00 SYMPOSIUM LUNCH.

Afternoon

Chairman: S. J. BUSH, ESQ.

14.30 "The action of light on colouring matters."
K. MCLAREN, B.Sc., F.R.I.C., F.S.D.C.
(*I.C.I. Dyestuffs Division, Manchester*).

15.00 "The rapid assessment of colour for routine storage testing."
J. D. CHESHIRE, B.Sc., A.R.I.C., and T. C. CORBY, B.Pharm., M.P.S.
(*Beecham Toiletry Division, Brentford*).

15.30 "The chemistry of synthetic dyes used in cosmetics."
J. C. BROWN, B.Sc., F.R.I.C. (*Ciba Clayton Ltd. Manchester*).

16.00 Symposium ends.

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.

OBITUARY

Dr. W. W. Myddleton

With the passing of Dr. Myddleton the Society has lost a valued member of high attainments and gentle culture. He was born in 1890, educated in Northern Ireland and graduated at Belfast University where he was awarded the degree of Doctor of Science. In his younger days he was a chemist at Crosfield, Warrington, where he built up a reputation as a soap chemist and gained a wide knowledge of oils and fats.

Subsequently he came to London and was for a number of years a lecturer in chemistry at Birkbeck College. During this period he extended his field to include mineral oils and became a Fellow of the Institute of Petroleum. Just prior to the 1939 war he received a senior appointment at the newly founded Coal Utilization Research Station but owing to happenings beyond his control the Research Station was abandoned. It was in 1940–41 that I was fortunate in getting him to join me at County Perfumery Co. Ltd. He stayed until 1955 when he retired at the age limit. During the ensuing years he published many notes and reports in the technical press. His great undertaking was to rewrite and bring up-to-date Vol. II of the book by R. S. Harry dealing with Cosmetic Materials, a labour which he carried out on his own and published in 1963.

He became a Member of the Society in 1952, was a Member of Council from 1956–58 and acted as Hon. Advertising Manager from 1957–59. His death occurred suddenly on 26th December 1965, but thankfully in peace.

As a man and colleague he was loved especially in that he was a gentleman of the first order, and his memory will be treasured in the years to come.

Robert H. Marriott.

He loves me... he loves me not... he loves me...

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