VOL XVII NO 1 8 JANUARY 1966

# Journal of the Society of Cosmetic Chemists

## Contents

Page

ORIGINAL SCIENTIFIC PAPERS

SUBJECT REVIEW ARTICLES

SOCIETY OF COSMETIC CHEMISTS OF GREAT BRITAIN

*fragrance of outstanding beauty adds the distinctive character— the individuality— that can bring success to a perfume or cosmetic...or a complete line!*

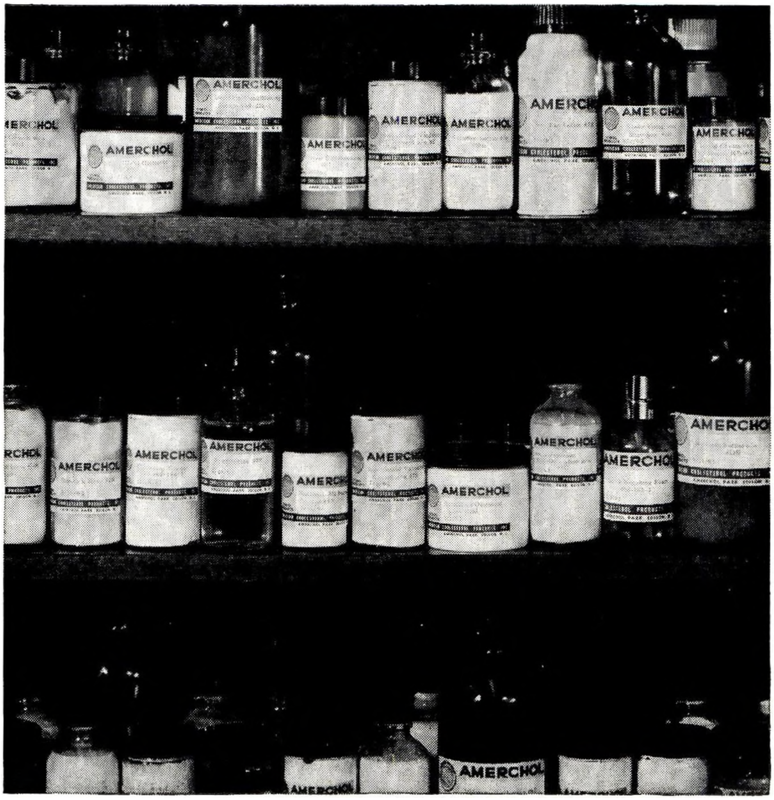
*Givaudan's demonstrated creative skill, its unusual variety of fragrant materials, its world-wide affiliations and its market know-how are all co-ordinated to bring you fragrances of unique new beauty and originality— made-to-measure for your success.*

Givaudan & Co. Ltd.

SYMBOL OF QUALITY

**WHYTELEAFE · SURREY · PHONE : UPPER WARLINGHAM 2241**

# INDEX TO ADVERTISERS


AMERCHOL

A Vital New
Pergamon Publication

**Advances in Biology of Skin**
Volume 6—Aging
Proceedings of the Symposium held at the University of Oregon Medical School, 1964
**Edited by W. Montagna,** *University of Oregon Medical School*

The progressive deterioration of his skin is one of the most direct indices of man's age. Changes occur at all levels in the skin, from the physicochemical properties of the connective tissue to the population density and the function of the adnexa. In spite of extensive and diversified studies, progress in our understanding of aging skin has been slow. This book brings together some of the varied disciplines which have been used in the study of aging phenomena, and covers morphology, biochemistry and physiology.

**Contents:**
Morphology of the aging skin: the cutaneous appendages; Effects of aging on the papillary body of the hair follicles and on the eccrine sweat glands; Age changes in the human melanocyte system; Nerve changes in aging skin; The effects of aging on the receptor organs of the human dermis; The anatomy of the human scalp; The effect of aging on the activity of the sebaceous gland in man; The effect of age on human eccrine sweating; Effect of aging on human dermis. Studies of thermal shrinkage and tension; Percutaneous absorption in aged skin; The effect of topical steroids on the aged human axilla; Alterations in human dermal fibrous connective tissue with age and chronic sun damage; Human cutaneous acid mucopolysaccharides: the effects of age and chronic sun damage; Temporal changes in collagen—aging or essential maturation?; Biophysical aspects of aging in connective tissue; The chemistry of elastin and its relationship to structure; Structure and metabolism of skin polysaccharides.
**Approx. 300 pages/Autumn 1965**
**Approx. 100s./Approx. $15.00.**

Offered for sale in the bookshops of

Robert Maxwell & Co. Ltd.
4/5 Fitzroy Square, London W1; Waynflete Building, Oxford; 2/3 Teviot Place, Edinburgh 1; 2/3 Richmond Street, Glasgow C1; 44-01 21st Street, Long Island City, New York 11101; 24 rue des Ecoles, Paris Ve; Kaiserstrasse 75, Frankfurt-am-Main; and all other reputable bookshops throughout the world.

# Food and Cosmetics Toxicology

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

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

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

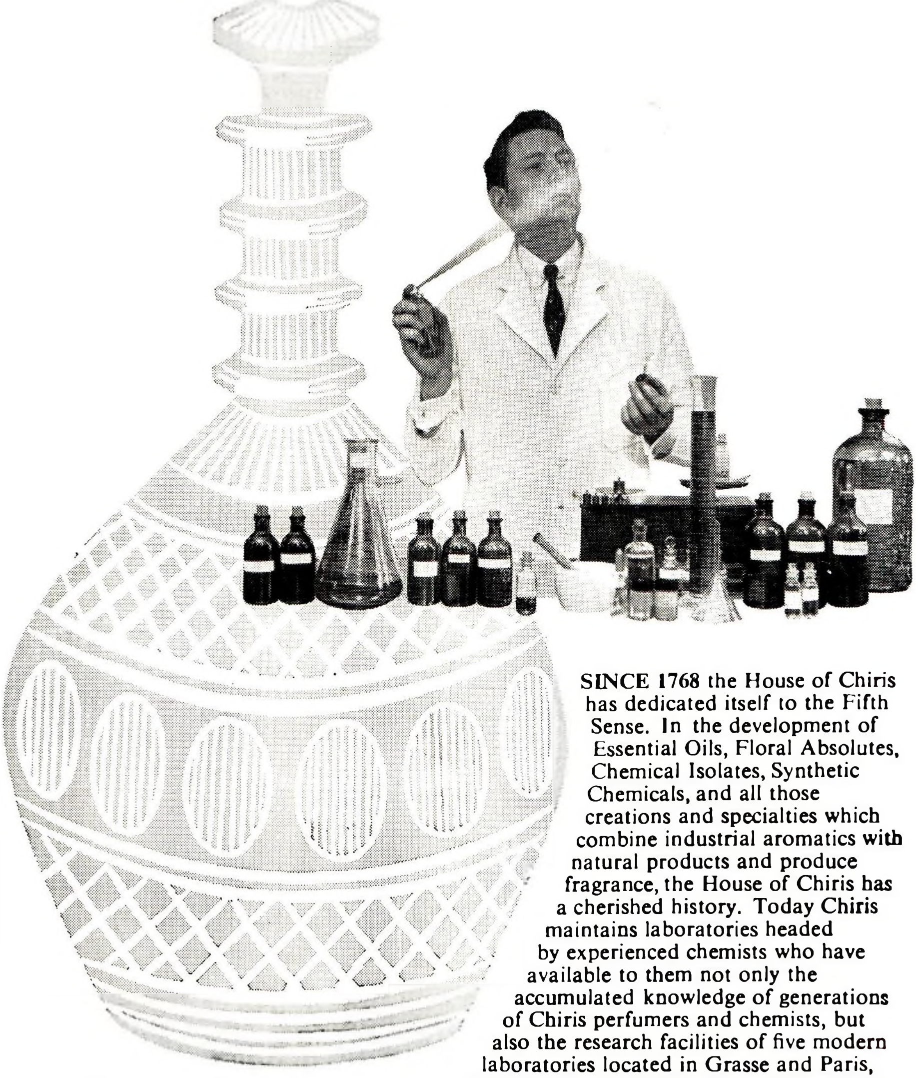
**Review Section :** provides information on papers dealing with the biochemical, pharmacological, toxicological, medical and veterinary aspects of the subject.

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

Summary of Toxicological Data

Letters to the Editor   Book Reviews   Forthcoming Papers

Bi-Monthly
*Write now for Specimen Copy and details of subscription rates*
**PERGAMON PRESS**
Headington Hill Hall, Oxford, England
44-01 21st Street, Long Island City, New York 11101, U.S.A.



# 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.**

**Determination of chlorinated phenols in powered deodorants:** S. Lee and N. A. Puttnam. *Journal of the Society of Cosmetic Chemists* **17** 3-8 (1966)

**Synopsis**—A rapid UV spectroscopic method is described for the determination of hexachlorophene in powdered personal deodorants. The method is based on the absorbance at 33.8 $\mathrm{Kcm}^{-1}$ (296 mμ) of an acidic methanol extract of the product. The standard deviation is ± 0.005% at the 0.5% hexachlorophene level.

The presence of a chloroxylenol is indicated by an increase in the absorbance at 35.8 $\mathrm{Kcm}^{-1}$ (279 mμ) and can be determined simultaneously. If the identity of the chloroxylenol is unknown, the use of an average $E_1$ value at 35.8 $\mathrm{Kcm}^{-1}$ only introduces serious error if the chloroxylenol should happen to be 4-chloro-2:5-dimethyl or 6-chloro-3:4-dimethyl phenol.

**Application of Attenuated Total Reflectance IR spectroscopy to toilet articles and household products, 2. Quantitative analysis:**
N. A. Puttnam, B. H. Baxter, S. Lee and P. L. Scott.
*Journal of the Society of Cosmetic Chemists* **17** 9-16 (1966)

**Synopsis**—The application of Attenuated Total Reflectance IR spectroscopy to the quantitative analysis of toilet articles and household products is described. The analyses were carried out by comparison with calibration curves prepared from standard samples. Examples are quoted of the determination of lauryl ether sulphate and salts of sulphated fatty alcohols in shampoos, the determination of glycerol in glycerine/sarcosinate solutions, the determination of ethanol in aqueous ethanol systems, the simultaneous determination of pyrophosphate and alkyl aryl sulphonate in a household cleaner and moisture in soap. The relative accuracy of these analyses was ± 1.5 to ± 3.0% and as each determination required less than 8 min they could be used for the routine control of such products.

**Cationic emulsifiers in cosmetics:** K. M. Godfrey.
*Journal of the Society of the Cosmetic Chemists* **17** 17-27 (1966)

**Synopsis**—The use of cationic surface active chemicals as emulsifiers in cosmetic products has been a relatively recent development. Their properties are reviewed and methods of making use of them are discussed. The sensitizing of emulsions to "break" on contact with surfaces to which they are applied has particular interest to the formulator of cosmetic products.

**Some principles and difficulties of topical treatment in dermatology:** G. Hodgson. *Journal of the Society of Cosmetic Chemists* **17** 29-44 (1966)

**Synopsis**—The majority of dermatological topical treatment is used for alleviation of symptoms. These arise from systemic disease, or are just temporary, or longer lasting, individual variations in functions of the skin from the physiological mean. The efficacy of established topical treatments is discussed, including the use of antiperspirants and detergent acne preparations.

Antipruritic agents usually act by anaesthetizing pain fibres or reducing bacterial degradation of protein to polypeptides, which provoke itching. Both local procaine-type anaesthetics and antibiotics, especially the 'mycin' group, are liable to cause sensitization.

Topical steroids used under occlusive polythene dressings to increase hydration and permeability in established eczema or psoriasis may cause severe local degeneration of collagen with epidermal thinning, skin stretching ('striae') and bruising, in addition to systemic absorption effects.

The treatment of melanosis with bleaching agents, or hydroquinone monobenzyl ether is clinically and cosmetically unsatisfactory, as is that of depigmentation with methoxy psoralens or disguising agents, such as dihydroxyacetone.

---

**The subjective assessment of the consistency of materials in relation to physical measurements:** G. W. Scott Blair.
*Journal of the Society of Cosmetic Chemists* **17** 45-56 (1966)

**Synopsis**—In all traditional, and even in some modern industries, the properties of materials and products are assessed by experts handling them. This is not in itself a bad thing but experts are becoming increasingly difficult to find and it is useful both for the craftsmen themselves and for those working in their absence to be able to compare such subjective assessments with physical measurements and chemical analyses. This paper is concerned with one group of "properties" commonly called "consistency." One must first ask whether the sensations perceived by the experts are themselves quantitatively measurable and, if not, how do we regard the judgements which they are undoubtedly able to make? A second question follows: By what combinations of stresses, strains and times do people assess consistency when they squeeze materials by hand? Are such combinations dimensionally similar to those which we use to define such physical properties as viscosity and elastic moduli? What mathematical and statistical techniques are required to describe the judgements offered?

Finally, the implications of psychorheology to the practical chemist or physicist working in a traditional industry are discussed.

# Journal of the Society of Cosmetic Chemists

## 1966

## VOL. XVII

# Journal of the Society of Cosmetic Chemists

VOL. XVII 1966

## THE SOCIETY OF COSMETIC CHEMISTS OF GREAT BRITAIN

## Committees for 1965-66

### SCIENTIFIC COMMITTEE

Dr. A. W. Middleton (*Chairman*)
Mr. S. J. Bush
Mr. A. Herzka
Dr. H. W. Hibbott
Mr. N. J. Van Abbé

### METHODS OF ANALYSIS SUBCOMMITTEE

Mr. S. J. Bush (*Chairman*)
Miss L. P. Torry (*Secretary*)
Mr. T. J. Bowditch
Mrs. D. M. Gabriel
Miss Gartside
Dr. H. W. Hibbott
Mr. W. R. Stone
Mr. C. Waterhouse

### TOXICOLOGY SUBCOMMITTEE

Mr. N. J. Van Abbé (*Chairman*)
Miss L. P. Torry (*Secretary*)
Mr. D. F. Anstead
Mr. W. H. Bull
Dr. L. Golberg
Mr. A. Herzka
Dr. H. W. Hibbott
Dr. J. J. Mausner
Mr. G. A. C. Pitt
Professor A. N. Worden

### EDUCATION COMMITTEE

Dr. M. Cantley (*Chairman*)
Dr. B. A. Scott (*Secretary*)
Mr. D. E. Butterfield
Mr. E. K. Clarke
Dr. T. J. Elliott
Dr. H. W. Hibbott

### MEMBERSHIP COMMITTEE

Mr. D. E. Butterfield (*Chairman*)
Mr. E. K. Clarke
Dr. A. W. Middleton

### PUBLIC RELATIONS COMMITTEE

Mr. A. Herzka (*Chairman*)
Mr. D. E. Butterfield (*Secretary*)
Mrs. H. Butler
Mr. C. Pugh
Mrs. D. L. Wedderburn

### PROGRAMME COMMITTEE

Mr. A. Herzka (*Chairman*)
Mr. D. E. Butterfield (*Secretary*)
Mr. S. J. Bush
Mrs. H. Butler
Dr. J. J. Mausner
Dr. A. W. Middleton
Mr. C. Pugh
Mr. N. J. Van Abbé

### BUDGETING COMMITTEE

Mr. R. E. Spate (*Chairman*)
Mr. R. Clark
Mr. G. A. C. Pitt

### HONORARY MEMBERSHIP COMMITTEE

Mr. S. J. Bush (*Chairman*)
Mr. A. Herzka
Dr. H. W. Hibbott
Mr. J. Pickthall
Mr. G. A. C. Pitt

### PUBLICATIONS COMMITTEE

Mr. A. Herzka (*Chairman*)

*J. Soc. Cosmetic Chemists* **17** 3-8 (1966)

# Determination of chlorinated phenols in powdered deodorants

S. LEE and N. A. PUTTNAM*

**Synopsis**—A rapid UV spectroscopic method is described for the determination of hexachlorophene in powdered personal deodorants. The method is based on the absorbance at 33.8 Kcm$^{-1}$ (296 m$\mu$) of an acidic methanol extract of the product. The standard deviation is ± 0.005% at the 0.5% hexachlorophene level.

The presence of a chloroxylenol is indicated by an increase in the absorbance at 35.8 Kcm$^{-1}$ (279 m$\mu$) and can be determined simultaneously. If the identity of the chloroxylenol is unknown, the use of an average $E^1_1$ value at 35.8 Kcm$^{-1}$ only introduces serious error if the chloroxylenol should happen to be 4-chloro-2:5-dimethyl or 6-chloro-3:4-dimethyl phenol.

## INTRODUCTION

Chlorinated phenols are frequently incorporated into personal deodorants as bacteriocides, the most commonly used being hexachlorophene [2:2$^1$-methylene-bis-(3:4:6-trichlorophenol)]. However, recent formulations have employed a chloroxylenol as an antiseptic agent in conjunction with hexachlorophene. Such compounds, in common with other phenols, show absorption maxima in the wavelength range 270 to 300 m$\mu$, the exact frequency being dependent upon the type and position of substituents within the aromatic ring. Under alkaline conditions the absorption maxima are shifted approximately 20 m$\mu$ towards longer wavelengths, due to the formation of a phenate ion. This shift is often used in the determination of phenols to reduce interferences from other components of the system. However, in "partially hindered phenols," such as hexachlorophene, ionisation is only complete in the presence of relatively high concentrations of alkali (1). Absorptions due to both the phenol and the phenate ion are detected in the presence of insufficient alkali.

Clements and Newburger (2) have described a UV spectroscopic method for the determination of hexachlorophene in soaps and cosmetic prepara-

---

*Research and Development Department, Colgate-Palmolive Limited, Manchester, 5.

tions. In their procedure, the hexachlorophene was extracted from the product with alkali and then isolated, by acidifying this extract, prior to the spectroscopic determination. A similar determination has been reported by Elvidge and Peutrell (3), which was based on the "difference" absorption at 312 mμ of the sample in a solution buffered at pH 8.0 and in a solution buffered at pH 1.4. Such procedures suffer from the disadvantage that deodorants usually contain aluminium compounds as antiperspirants, which, on treatment with alkali, produce a gelatinous precipitate of aluminium hydroxide with is difficult to remove. In the present communication, which describes a rapid method for the determination of hexachlorophene in powdered personal deodorants, this difficulty is overcome by the use of acidic methanol. The method is based on the absorbance at 33.8 $\mathrm{Kcm}^{-1}$ (296 mμ) of an acidic methanol extract of the product. The presence of a chloroxylenol is readily detected at 35.8 $\mathrm{Kcm}^{-1}$ (279 mμ) and is determined simultaneously.

## Experimental

The spectra were determined on a *Unicam* SP 700 recording UV/near IR spectrophotometer in 10 mm silica cells.

The reference data for hexachlorophene and the chlorinated xylenols was obtained by weighing approx. 100 mg of the phenol into a 50 ml graduated flask and diluting to volume with N/10 methanolic HCl (prepared by adding 100 ml of N/1 hydrochloric acid to a litre graduated flask and diluting to volume with *Spectrosol* grade methanol). 1 ml of this solution was then pipetted into a 100 ml graduated flask and diluted to volume with solvent. The spectrum of this solution was then recorded against a solvent blank over the wavelength range 41 $\mathrm{Kcm}^{-1}$ (224 mμ) to 30 $\mathrm{Kcm}^{-1}$ (333 mμ). A tangent base-line to the absorptions was then drawn and the $E_1^1$ values, i.e. the absorbance for a 1% solution in a 10 mm cell, at 33.8 $\mathrm{Kcm}^{-1}$ (296 mμ) and 35.8 $\mathrm{Kcm}^{-1}$ (279 mμ) calculated.

For the analysis of a powdered deodorant, 0.5 g of the sample was weighed into a 50 ml centrifuge tube and 25 ml of N/10 methanolic HCl added. The contents of the tube were agitated for 3 min with a glass rod and then centrifuged at 3000 rpm for 2 min. The upper layer was decanted into a 100 ml graduated flask and the residue re-extracted with a further 2 × 25 ml portions of solvent. The methanolic extracts were combined in the graduated flask and made up to volume with solvent. The spectrum of this solution was then recorded, as described above, and the $E_1^1$ values at 33.8 $\mathrm{Kcm}^{-1}$ and 35.8 $\mathrm{Kcm}^{-1}$ similarly calculated.

If the ratio of the $E_1^1$ values at 33.8 and 35.8 Kcm$^{-1}$ was less than 2.15, chloroxylenols were absent and the hexachlorophene content was calculated from the equation—

$$\%\ \text{w/w hexachlorophene} = 100 \times E^{S}_{33.8}/E^{H}_{33.8}$$

where $E^{S}_{33.8}$ and $E^{H}_{33.8}$ are the respective $E_1^1$ values of the sample and hexachlorophene at 33.8 Kcm$^{-1}$. However, if this was not the case the following simultaneous equations were solved for the hexachlorophene and chloroxylenol contents.

$$E^{S}_{33.8} = E^{X}_{33.8}(x) + E^{H}_{33.8}\,(h)$$

and

$$E^{S}_{35.8} = E^{X}_{35.8}\,(x) + E^{H}_{35.8}\,(h)$$

where $E^{S}_{35.8}$ is the $E_1^1$ value of the sample at 35.8 Kcm$^{-1}$, $E^{X}_{33.8}$ and $E^{X}_{35.8}$ are the $E_1^1$ values of the chloroxylenol at 33.8 and 35.8 Kcm$^{-1}$ respectively, $E^{H}_{35.8}$ is the $E_1^1$ value of hexachlorophene at 35.8 Kcm$^{-1}$ and (x) and (h) are the respective concentrations of chloroxylenol and hexachlorophene.

## RESULTS AND DISCUSSION

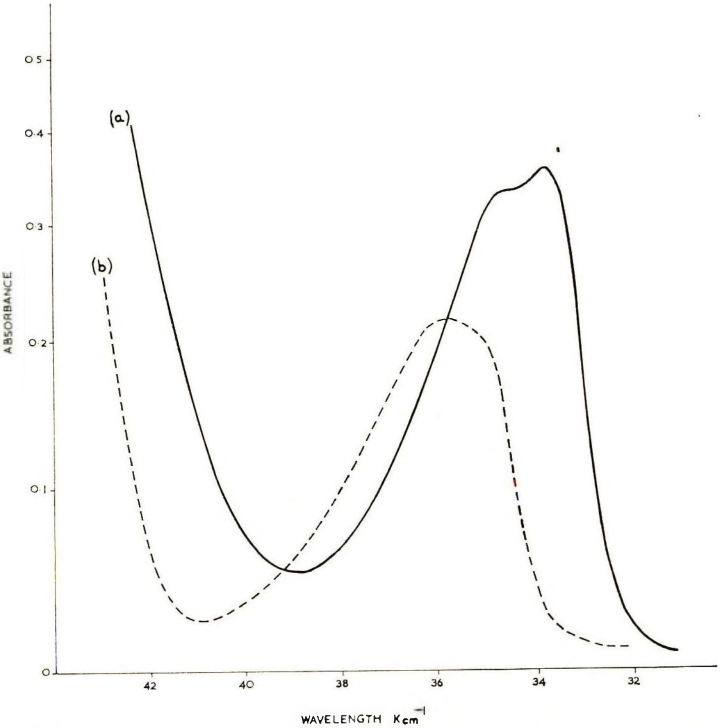


*Figure 1* Spectra of hexachlorophene (a) and 4-chloro 3:5-dimethylphenol (b) in N/10 methanolic HCl.

*Fig. 1* shows the absorption spectra of hexachlorophene and chloroxylenol (4-chloro-3:5-dimethylphenol) in N/10 methanolic HCl solvent. The former showed an absorption maxima at 33.8 Kcm$^{-1}$ while the maxima for the latter occurred at 35.8 Kcm$^{-1}$. It was found that the maxima for other chloroxylenols occurred close to this value, the actual range being 35.5 to 35.9 Kcm$^{-1}$ (281.5 to 279 mμ).

The $E_1^1$ values for various chlorinated phenols at 33.8 and 35.8 Kcm$^{-1}$ in N/10 methanolic HCl are recorded in *Table I.*

Table I $E_1^1$ values at 33.8 and 35.8 Kcm$^{-1}$ for chlorinated phenols in N/10 methanolic HCl.

| Phenol | $E_1^1$ value<br>at 33.8 Kcm$^{-1}$ | <br>at 35.8 Kcm$^{-1}$ |
|---|---|---|
| Hexachlorophene | 138.4 | 63.8 |
| 4-Chloro-3:5-dimethyl | 4.05 | 95.5 |
| 4-Chloro-2:3-dimethyl | 7.7 | 101.0 |
| 4-Chloro-2:5-dimethyl | 20.2 | 138.8 |
| 4-Chloro-2:6-dimethyl | 3.2 | 98.8 |
| 2-Chloro-3:5-dimethyl | 2.72 | 103.5 |
| 6-Chloro-3:4-dimethyl | 21.7 | 166.0 |

Spectrum (a) in *Fig. 2* is of the N/10 methanolic HCl extract of a powdered deodorant formulated to contain 0.5% w/w hexachlorophene and 0.12% w/w 4-chloro-3:5-dimethylphenol. In spectrum (b), which was the extract of a product formulated to contain hexachlorophene, the decreased absorption at 35.8 Kcm$^{-1}$ confirmed the absence of a chloroxylenol.

From a series of replicate determinations performed on a powdered deodorant, formulated to contain 0.5% w/w hexachlorophene, the standard deviation for the determination of hexachlorophene was found to be ± 0.005%. The results obtained for a powdered deodorant formulated to contain 0.5% w/w hexachlorophene and 0.12% 4-chloro-3:5-dimethylphenol are recorded in *Table II.*

Table II Hexachlorophene and 4-chloro-3:5-dimethylphenol content of powdered deodorant

| Sample No. | % w/w hexachlorophene | % w/w 4-chloro-3:5-dimethyl phenol |
|---|---|---|
| 1 | 0.472 | 0.117 |
| 2 | 0.486 | 0.119 |
| 3 | 0.480 | 0.115 |
| 4 | 0.487 | 0.125 |
| 5 | 0.479 | 0.120 |

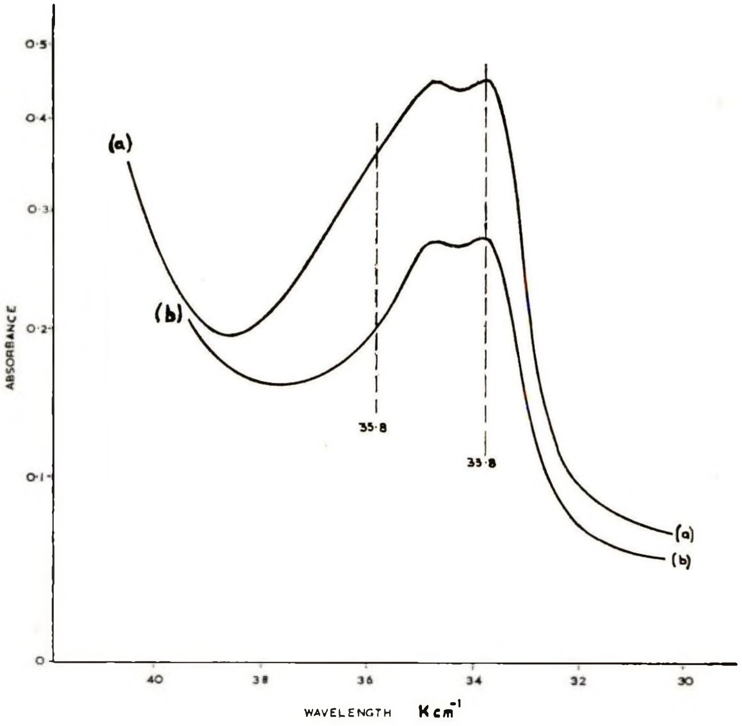


*Figure 2* Spectra of N/10 methanolic HCl extracts of powdered deodorants.

The spectra shown in *Fig. 2* clearly showed that under the conditions employed for the analysis, the acidity was sufficient to prevent formation of a phenate ion. Under other conditions the varying degree of alkalinity in a product would have produced variable amounts of phenate ion and hence non-reproducible analytical results. The use of an acidic solvent prevented the gelatinous precipitation of aluminium hydroxide, the only insoluble material being talc which was removed by centrifuging. The completeness of extraction of the phenols by the described procedure was shown by the absence of absorptions in the wavelength range 32.0 to 40 Kcm$^{-1}$ for a fourth extract.

The use of a tangent base-line to determine the corrected absorbances at 33.8 and 35.8 Kcm$^{-1}$ allowed for extraneous background absorptions due to other components of the product. This can be seen by comparing *Figs. 1* and *2*.

For a product which has been shown to contain a chloroxylenol, but the identity of which is unknown, the value of $E^{X}_{35.8}$ can be taken as 100 to determine the concentration of the chloroxylenol. This procedure will only introduce a serious error if the component happens to be 4-chloro-2:5-dimethyl or 6-chloro-3:4-dimethylphenol.

(*Received: 29th June 1965*)

REFERENCES

(1) Coggeshall, N. D. and Glesser, A. S. *J. Am. Chem. Soc.* **71** 3150 (1949).
(2) Clements, J. E. and Newburger, S. H. *J. Assoc. Offic. Agr. Chemists* **37** 190 (1954).
(3) Elvidge, D. A. and Peutrell, B. *J. Pharm. Pharmacol.* **13** Suppl. 111T (1961).

*J. Soc. Cosmetic Chemists* **17** 9-16 (1966)

# Application of Attenuated Total Reflectance IR spectroscopy to toilet articles and household products, 2.—Quantitative analysis

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

*Presented in part at the XIth Colloquium Spectroscopicum Internationale, Belgrade 1963.*

**Synopsis**—The application of Attenuated Total Reflectance IR spectroscopy to the quantitative analysis of toilet articles and household products is described. The analyses were carried out by comparison with calibration curves prepared from standard samples. Examples are quoted of the determination of lauryl ether sulphate and salts of sulphated fatty alcohols in shampoos, the determination of glycerol in glycerine/sarcosinate solutions, the determination of ethanol in aqueous ethanol systems, the simultaneous determination of pyrophosphate and alkyl aryl sulphonate in a household cleaner, and moisture in soap. The relative accuracy of these analyses was ± 1.5 to ± 3.0% and as each determination required less than 8 min they could be used for the routine control of such products.

## INTRODUCTION

The application of Attenuated Total Reflectance IR spectroscopy to the qualitative identification of components in toilet articles and household products has been described previously (1), together with the principle of the technique.

From the quantitative aspect, although Beer's law is not valid for reflection spectra, it is still a fair approximation (2) and several reports have appeared of relationships having been established between formal "absorbance" and concentration. Fahrenfort (3) showed that such a relationship existed for the 907 and 992 $cm^{-1}$ absorptions of decene-1 in *Nujol,* while Wilhite and Ellis (4) described the determination of the

---

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

nitrate ion in aqueous solutions. Such a determination was also reported by Katlafsky and Keller (5), who extended the technique to the determination of the sulphate ion and 2-methyl-2-nitro-1-propanol in aqueous solutions.

In this communication we wish to describe the application of ATR to the quantitative determination of relatively major components in various types of toilet articles and household products.

## Experimental

The ATR spectra were recorded on a *Unicam* SP 200 IR spectrometer using a TR-3 ATR attachment, manufactured by Research and Industrial Instruments Co. An Irtran II prism was employed as the analysing crystal and the reference beam was attenuated to give an absorbance value of approximately 0.1 at a wavelength where the sample showed no absorption.

Liquid samples were introduced with a syringe through the filler-ports into the cell formed by fitting the backing plate, with a *Teflon* seal, to the prism mount, care being taken to ensure that there were no air bubbles in the cell. Viscous liquids were poured on to the back face of the prism, held in a horizontal position, and the backing plate then clamped in position. In the case of soap samples, these were shredded on a cheese grater and a portion of the shredded samples pressed against the back face of the prism.

For the preparation of calibration curves the ATR spectra of a series of standard samples (in most cases these were prepared by dilution of a reference concentrated sample) were recorded. The "absorbance" of the characteristic peak was measured, using a tangent base-line, for each standard and plotted against the % w/w concentration of the component. For the analysis of a sample, the ATR spectrum was recorded on the sample "as is" by a similar procedure to that used to prepare the appropriate calibration curve.

## Results and Discussion

The angle selected for each analysis was that which gave the greatest absorbance value but still produced absorption peaks which did not appear distorted. It varied for each type of sample but was within the range 33 to 40°. To eliminate any possible backlash in the ATR attachment the angle setting was always made by approaching from low angle side.

For most liquid samples a linear calibration curve of "absorbance" against % w/w concentration was obtained. However, in the case of ethanol-water systems there was a slight deviation from linearity at the higher concentration.

The determination of lauryl ether sulphate in a shampoo, a typical spectrum of which is shown in *Fig. 1,* was based on the "absorbance" of the sulphate absorption at ca. 1220 cm$^{-1}$, using a tangent base-line drawn between 990 and 1330 cm$^{-1}$. It was found that the standard deviation of the method was ± 0.2% at the 17.0% w/w level of active ingredient. A comparison of the results from the ATR method with those obtained by cationic titration with cetyl pyridinium chloride and bromophenol blue, as indicator, for the lauryl ether sulphate content of a series of shampoos is recorded in *Table I.*

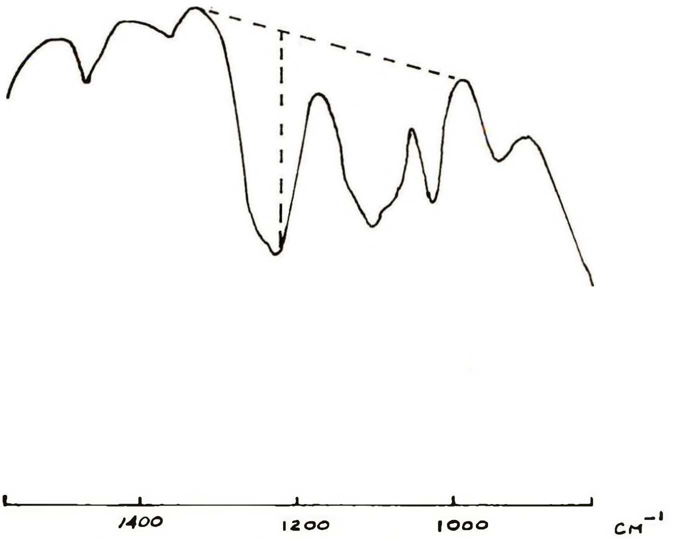


*Figure 1.* Determination of lauryl ether sulphate in a shampoo.

Table I Lauryl ether sulphate content of a series of shampoos

| Method | % w/w lauryl ether sulphate | | | | | | |
|---|---|---|---|---|---|---|---|
| ATR | 16.4 | 19.0 | 16.8 | 16.6 | 16.8 | 17.2 | 19.1 |
| Cationic titration | 16.26 | 19.05 | 16.71 | 16.67 | 16.95 | 17.11 | 19.0 |

This method has been extended to the determination of sodium or triethanolamine salts of sulphated fatty alcohols in shampoos, and the same degree of accuracy was obtained.

*Table II* quotes the results obtained from an ATR procedure for the determination of glycerol in a series of glycerine/sarcosinate intermediate solutions. These results have been compared with those obtained by sodium periodate oxidation of the glycerol followed by titration of the liberated formic acid.

Table II Glycerol content of glycerine/sarcosinate solutions

| Method | % w/w glycerol | | | | |
|---|---|---|---|---|---|
| ATR | 29.8 | 30.0 | 29.9 | 30.1 | 30.0 |
| Oxidation with periodate | 29.57 | 30.12 | 30.08 | 30.02 | 29.93 |

The ATR method was based on the "absorbance" of the glycerol absorption at 1045 $cm^{-1}$ and the analysis was carried out at an angle of 35°. It was found that duplicate determinations agreed to within 0.1%.

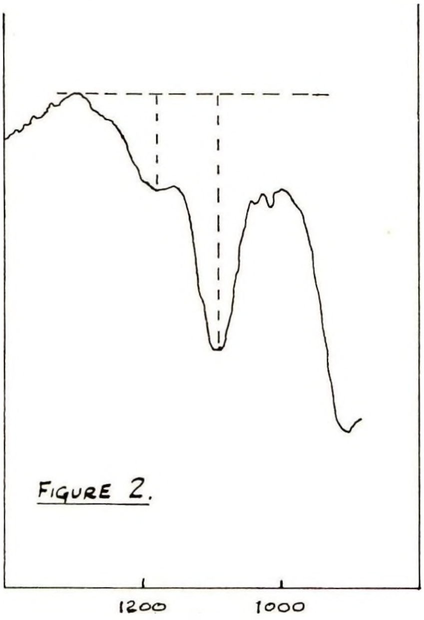


FIGURE 2.

Determination of pyrophosphate and alkyl aryl sulphonate in household cleaner.

The ethanol content of after-shave lotions was determined from the "absorbance" of the ethanol absorption at 1045 $cm^{-1}$, using an angle of 40°. The standard deviation for this anlysis was ± 1.5% at the 50% w/w ethanol level. This procedure was also used as an alternative method for determining the ethanol content of aqueous distillates obtained from light duty detergent products. The method was superior to that which involves measurement of specific gravity and comparison with specific gravity tables for aqueous/ethanol systems in that it was quicker, the volume of sample required was much less, and a constant temperature bath at the correct temperature was not needed.

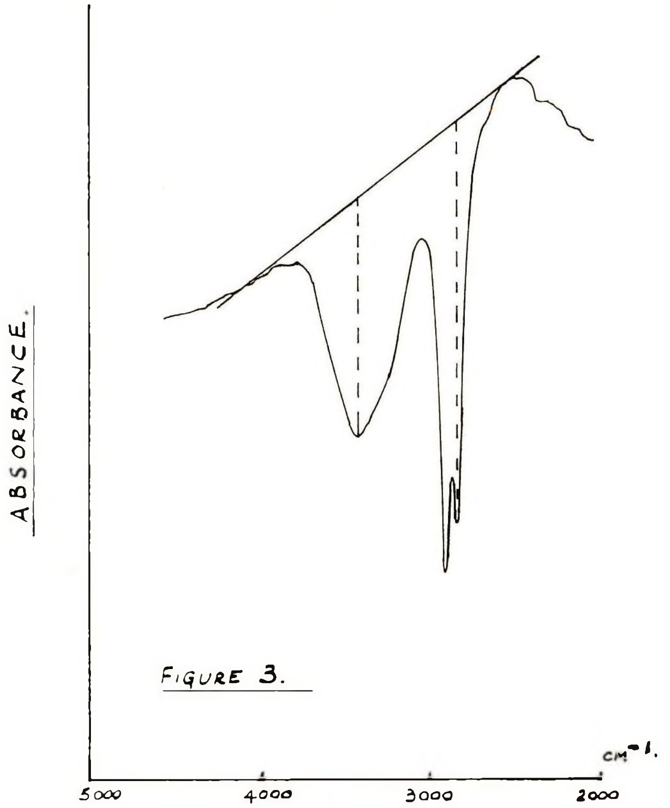


FIGURE 3.

Determination of moisture in soap.

The ATR method for the simultaneous determination of pyrophosphate and alkyl aryl sulphonate, expressed as % w/w $NaSO_3$- grouping, in a household cleaner, the spectrum of which is shown in *Fig. 2,* was based on the respective absorptions at 1090 and 1180 $cm^{-1}$. The analysis was carried out at an angle of 35° and a spot background was taken at 1300 $cm^{-1}$ instead of employing the tangent base-line procedure. The results for repeat analyses of a sample of this cleaner are recorded in *Table III.*

Table III Repeat determinations of pyrophosphate and alkyl aryl sulphonate in a household cleaner

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| % pyrophosphate | 10.0 | 10.1 | 10.1 | 9.9 | 10.1 | 10.1 | 9.8 |
| % $NaSO_3$- | 2.15 | 2.0 | 2.1 | 2.1 | 2.05 | 2.0 | 2.15 |

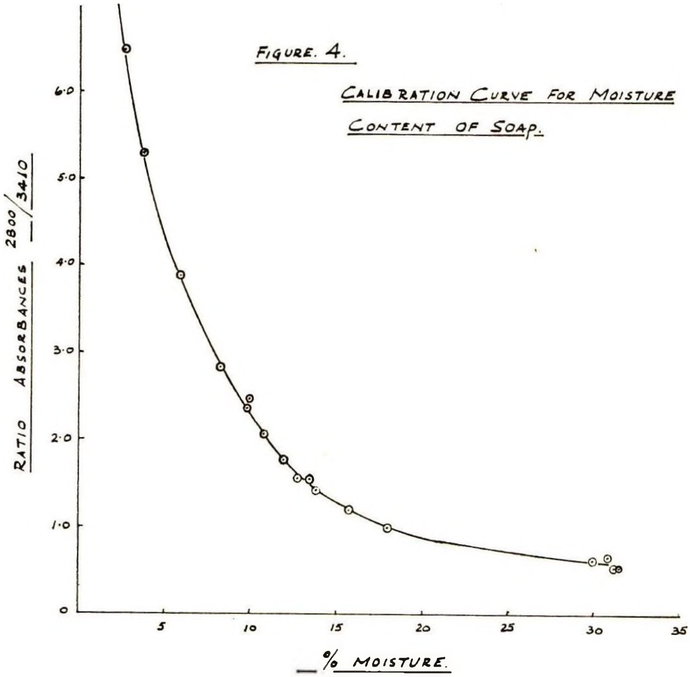


FIGURE. 4.

CALIBRATION CURVE FOR MOISTURE CONTENT OF SOAP.

ATR spectra of soaps, an example of which is shown in *Fig. 3,* showed absorptions at 2800 and 2910 cm$^{-1}$ due to the alkyl chain of the fatty acid salts and a broad absorption at 3410 cm$^{-1}$ due to water. Other hydroxyl-containing components in the soap, e.g. glycerol, would also absorb in this latter region. However, it was assumed that at the low concentrations at which they would be present in the soap their contributions to the absorption at 3410 cm$^{-1}$ could be neglected and it could be considered as a binary mixture of water and a fatty acid salt. Water also showed an absorption at ca. 1640 cm$^{-1}$, which was free from interference by other components containing hydroxyl, but the intensity of this band was much weaker than that of the 3410 cm$^{-1}$ absorption. A direct measurement of the "absorbance" of the water absorption at ca. 3410 cm$^{-1}$ was not possible since for each sample there is non-reproducible contact between the sample and the prism. This effect was found to give variations of as much as ± 12% in the "absorbance" values for repeat determinations on the same sample. As the ratio of the "absorbance" at 2800 cm$^{-1}$ to that at 3410 cm$^{-1}$ would not be affected by the amount of contact, the calibration curve was obtained by plotting this ratio against the % w/w moisture content and is shown in *Fig. 4.* Standard soap samples were shredded and their moisture contents determined by Dean and Starke distillation with 95/120° petroleum ether. Simultaneously, the ATR spectrum of each sample was recorded in triplicate, at an angle of 33°, and the ratio of "absorbances" calculated using a tangent base-line drawn between 2500 and 4000 cm$^{-1}$. In *Table IV* are recorded the results obtained for several samples of soap. These moisture contents are compared with those obtained by loss in weight, at reduced pressure, under an IR heater. By the latter method the results are in fact the percentage volatiles but for these samples they closely approximate to the moisture content.

Table IV
Moisture content of soap samples, (a) by ATR method; (b) by loss in weight at reduced pressure under an IR heater.

| Sample no. | % w/w moisture | |
|---|---|---|
| | (a) | (b) |
| 1 | 12.4 | 12.8 |
| | 12.9 | 12.9 |
| | 13.0 | 12.9 |
| | 12.5 | 13.2 |
| 2 | 14.3 | 14.0 |
| | 13.9 | 14.0 |
| | 14.0 | 14.3 |
| | 14.2 | |
| 3 | 13.6 | 13.8 |
| | 13.7 | 13.4 |
| | 13.4 | 13.7 |
| | 13.5 | 13.7 |
| | 13.5 | 13.5 |
| | 9.6 | 9.3 |
| | 9.5 | 9.7 |
| | 9.7 | 9.7 |
| | 9.6 | 9.5 |

It was found that for the ATR method the standard deviation was ± 0.25% at the 13.0% w/w moisture level.

The examples quoted above show the type of components in various products that can be determined directly by the ATR method. It should be pointed out that the component, or components, determined were relatively major ones, being at least 5% w/w concentration. A further point is that these analyses, which required less than 8 min per determination, could be used for the routine control of such products with the added advantage that a permanent record of the analysis is also obtained.

(*Received: 16th September 1965*)

REFERENCES

(1) Puttnam, N. A., Lee, S. and Baxter, B. H. *J. Soc. Cosmetic Chemists* **16** 607 (1965).
(2) Fahrenfort, J. Xth Colloquium Spectroscopicum Internationale, Maryland, 1962.
(3) Fahrenfort, J. *Spectrochim. Acta* **17** 698 (1961).
(4) Wilhite, R. N. and Ellis, R. F. *Appl. Spectry.* **17** 168 (1963).
(5) Katlafsky, B. and Keller, R. E. *Anal. Chem.* **35** 1665 (1963).

*J. Soc. Cosmetic Chemists* **17** 17-27 (1966)

# Cationic emulsifiers in cosmetics

K. M. GODFREY*

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

**Synopsis**—The use of cationic surface active chemicals as emulsifiers in cosmetic products has been a relatively recent development. Their properties are reviewed and methods of making use of them are discussed. The sensitizing of emulsions to "break" on contact with surfaces to which they are applied has particular interest to the formulator of cosmetic products.

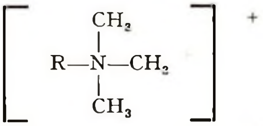
## INTRODUCTION

Surface active chemicals are conveniently classified as anionic, nonionic, cationic or ampholytic depending upon their ionization properties in solution. Molecules, of surface active chemicals which ionize, are anionic or cationic according to which ion contains the hydrophobic grouping.

Compounds such as soaps, alkyl sulphonates, alkyl aryl sulphonates, salts of sulphated alcohols, etc. are anionic as the negative ion contains the hydrophobic, long chain grouping, e.g.

| | | |
|---|---|---|
| $(CH_3.(CH_2)_{16}\,COO)^-$ | $Na^+$ | sodium soap of fatty acid |
| $(CH_3.(CH_2)_{15}\,OSO_3)^-$ | $Na^+$ | sodium cetyl sulphate |

When the ion containing the hydrophobic, long chain group, is positive the compounds are cationic, e.g.



$$\left[ R-\overset{\displaystyle CH_2}{\underset{\displaystyle CH_3}{N}}-CH_2 \right]^+ \quad X^-$$

quaternary ammonium salt

$$(CH_3.(CH_2)_{17}.NH_3)^+ \quad X^-$$

amine salt

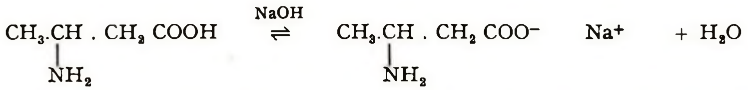
---

*Armour Hess Chemicals Ltd., Leeds, Yorks.

Ethoxylated phenols and fatty acids are examples of surface active compounds which do not ionize and so are classed as nonionic.

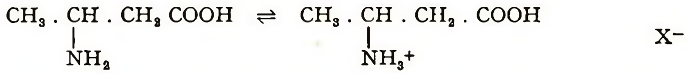
| $C_9H_{19}.C_6H_4.O(CH_2.CH_2.O)_xH$ | $C_{17}H_{35}COO(CH_2CH_2O)_xH$ |
|---|---|
| ethoxylated nonyl phenol | ethoxylated fatty acid |

The amphoteric, surface active chemicals contain hydrophobic groupings which may be anionic or cationic depending upon the conditions to which the material is subjected. In alkaline solution a salt of an acid grouping is formed and the molecule acts as an anionic surface active material.



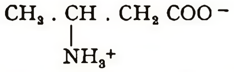
$$CH_3.\underset{NH_2}{\underset{|}{CH}}.CH_2\,COOH \overset{NaOH}{\rightleftharpoons} CH_3.\underset{NH_2}{\underset{|}{CH}}.CH_2\,COO^- \quad Na^+ \quad + H_2O$$

whilst in acid solution an amine salt is formed and the molecule acts as a cationic surface active material



$$CH_3.\underset{NH_2}{\underset{|}{CH}}.CH_2\,COOH \rightleftharpoons CH_3.\underset{NH_3^+}{\underset{|}{CH}}.CH_2.COOH \quad X^-$$

At its iso-electric point the molecule exists as an "internal salt" or Zwitterion



$$CH_3.\underset{NH_3^+}{\underset{|}{CH}}.CH_2\,COO^-$$

The use of anionic and nonionic surface active chemicals in the cosmetic industry, both as detergents and emulsifying agents, is well established but the use of cationic chemicals has developed rather more recently. One reason for this is that, in general, cationic materials of sufficiently high purity for the cosmetic chemist, have not been available in commercial quantities and at economical prices. In recent years, however, new cationic chemicals have become available and their improved purity means that the cosmetic chemist may now seriously consider making use of their unique properties. Du Brow (1) has summarized the types of quaternary ammonium compounds available and quotes $LD_{50}$ figures as high as 2000 mg/k and correspondingly low eye irritation values.

## QUATERNARY AMMONIUM COMPOUNDS

The quaternary ammonium compounds have been used in the cosmetic industry for a considerable time, mainly because of their germicidal properties. There are a large variety of materials available and a large number of hydrophobic groups have been used. The long chain alkyl quaternaries derived from fatty raw materials are among the most interesting materials. *Table I* summarizes the properties of a series of alkyl trimethyl ammonium chlorides and di-alkyl dimethyl ammonium chlorides.

Table I
Properties of alkyl ammonium chlorides

| Length or source of alkyl chain | Surface tension (dynes/cm) | Phenol coefficients at 37°C | |
|---|---|---|---|
| | 25°C 0·1% | *S. Aureus* | *E. Coli* |
| Mono C.12 trimethyl | 33 | 250 | 300 |
| ,, C.16 ,, | 34 | 415 | 300 |
| ,, C.18 ,, | 34 | 185 | 165 |
| Dicoco dimethyl | 30 | 430 | 270 |
| Dihydrogenated tallow dimethyl | 37 | — | — |

The use of quaternary ammonium compounds in cosmetic formulations is limited by their low compatibility with anionic surface active chemicals and certain other chemicals, e.g. sodium citrate, zinc salts, etc. Lawrence (2) gives a useful list of cationic compatible and incompatible materials. The list of incompatible materials could also include pectins, gum tragacanth, and sodium carboxymethyl cellulose. These materials may be looked upon as sensitizing agents to cationic systems (3). Precipitation of an anionic/cationic complex is normally indicated by cloudiness of a solution, but some complexes are water-soluble and others are easily solubilized by an excess of either constituent. It is, therefore, always necessary to check for absence of incompatibility in a product by measuring specific activity. This is particularly important in formulae utilizing the bactericidal activity of quaternary ammonium compounds, and it should never be assumed that the activity of the product will be equivalent to the content of quaternary incorporated.

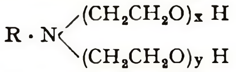
Addison and Furmidge (4) working on surface active chemicals to disperse grease and suint from animal fleece, studied the interfacial activity and soap compatibility of several series of quaternary ammonium compounds. They found that flocculation of suspended matter and low soap compatibility resulted when alkyl chains of more than fourteen carbon atoms were used. The $C_{14}$ derivatives, however, have good suspending power and soap compatibility. They also showed that the associated anion affects the properties of the cation. In the series $Cl^-$, $Br^-$, $I^-$ they found that each change of anion resulted in a change of overall properties equivalent to an increase in the alkyl chain of the cation of two carbon atoms, i.e. octadecyl pyridinium chloride $\equiv$ hexadecyl pyridinium bromide $\equiv$ tetradecyl pyridinium iodide. Most of the work was with pyridinium compounds but results with alkyltrimethyl quaternaries gave similar results.

More recently Shibe and Hanson (5) have emphasized the importance of the effect of the anion associated with quaternary ammonium cations. They have compared several properties of the chloride, saccharinate and phthalimidate salts of the alkyl ($C_{12}$-$C_{16}$), dimethyl, benzyl ammonium cation. The heat stability and the anionic compatibility of the compounds vary considerably with the anions for a given alkyl chain.

*Ethoxylated amines and their salts*

The tertiary amines produced by the reaction of ethylene oxide with aliphatic primary amines form related materials varying (a) in length of aliphatic chain, (b) in degree of ethoxylation.

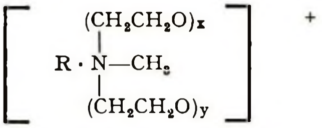
These chemicals are represented by the following general formula:—



$$R \cdot N \begin{matrix} \diagup (CH_2CH_2O)_x\,H \\ \diagdown (CH_2CH_2O)_y\,H \end{matrix}$$

R=alkyl chain ($C_{12}$ – $C_{18}$)

Ethoxylated amines can form salts with acids, and may be quaternized to produce ethoxylated quaternary ammonium compounds of general formula:—



$$\left[ \begin{matrix} & (CH_2CH_2O)_x \\ & | \\ R \cdot & N—CH_3 \\ & | \\ & (CH_2CH_2O)_y \end{matrix} \right]^+ X^-$$

R=alkyl chain ($C_{12}$ – $C_{18}$)

The polyglycol chains in these compounds increase the water solubility and general compatibility of the cation, so that in general, these cationic surface active chemicals have a greater tolerance for other chemicals.

Some properties of the series of stearyl amine derivatives are shown in *Table II*. It can be seen that the activity at the air/water interface, as measured by reduction in surface tension, is greatest for the 5 mol ethoxylate and reduces as the degree of ethoxylation is increased, and the material becomes increasingly water-soluble. Greatest activity, as measured by reduction in Canvas disc wetting time, does not occur until the 10 mol ethoxylate is reached.

Table II

Properties of ethoxylated stearyl amines

| Mol of ethylene oxide per mol of amine | Surface tension (dynes/cm) 0·1% | 1·0% | Canvas disc wetting time (6) 0·1% | 1·0% | Average mol. wt. |
|---|---|---|---|---|---|
| 5* | 34 | (gell) | 360 | (gell) | 495 |
| 5† | 34 | 33 | 226 | 12 | 482 |
| 15† | 41 | 40 | 157 | 27 | 925 |
| 50* | 49 | 47 | 360 | 360 | 2470 |

*Distilled $C_{18}$ derivatives.
†Tallow derivatives.

In this series, the properties of the molecule are varied from strongly lyophilic to strongly hydrophilic, or in the terms of the HLB system of emulsifier classification introduced by Griffin (7,8), from low to high HLB value. One therefore has related chemicals of varying degrees of hydrophilic character which form a useful series of emulsifiers for producing w/o or o/w emulsions of many materials.

### *Ethoxylated quaternary ammonium compounds*

The ethoxylated quaternary ammonium compounds are more water-soluble than the corresponding amine derivatives as they have the solubilizing effects of both the polyoxyethylene groups and the ionizing groups in the same molecule. For example, a stearyl amine condensate with two mol of ethylene oxide is water-insoluble whilst the quaternary ammonium compounds derived from this amine by reaction with methyl chloride is water-soluble. The amine could, of course, be made water-soluble by forming the soluble salt, e.g. acetate, but these salts are less compatible and more pH sensitive than the quaternary derivatives. *Table III* details the properties of two ethoxylated quaternary ammonium compounds derived from stearyl amine.

Table III
Properties of ethoxylated quaternary ammonium salts derived from ethoxylated stearyl amines.

| Mol of ethylene oxide per mol of quaternary | Surface tension dynes/cm 0·1% | 1·0% | Canvas disc wetting time 0·1% | 1·0% | Average mol. wt. |
|---|---|---|---|---|---|
| 2 | 41·4 | 38·3 | — | 44 | 422 |
| 15 | 49·1 | 48·7 | — | 73 | 994 |

## ADSORPTION PROPERTIES OF CATIONIC SURFACE ACTIVE CHEMICALS

Most solid non-conducting surfaces have been found to carry a negative charge under normal conditions, e.g. glass, hair, skin and most plastics. As the hydrophobic part of the cationic surface active chemical is, by definition, positively charged, it is to be expected that there will be a strong attraction between these cations in solution and a suitable surface presented to it. The cation will be precipitated on to the surface, and hence it will be removed from the liquid system in which it was initially dissolved.

Tamamushi and Tomaki (9) recently illustrated the strong adsorption of quaternary ammonium compounds onto aluminium oxide. They showed that dodecyl ammonium chloride followed an "L" type adsorption isotherm, normally associated with materials having high surface and low solvent affinity. The anionics, in general, follow an "S" type isotherm. At their C.M.C.'s Tamamushi and Tomaki showed the relative adsorption of dodecyl ammonium chloride and sodium dodecyl sulphate to be in the ratio of 8 : 1.

The property of strong adsorption by solid surfaces is of considerable value to the cosmetic chemist.

The qualitative effects of adsorption have been recorded and used in industry, particularly as a means of causing a surface in contact with an aqueous system to become hydrophobic and so to impart corrosion resistance, dropwise condensation of vapour, oil wettability, etc. Large quantities of cationic surface active chemicals are used in ore flotation, pigment wetting and corrosion inhibition. In the cosmetic industry the use of quaternaries (10), and more recently ethoxylated fatty amines (11-13) as conditioning agents in hair product formulations has been reported, and this action depends upon the adsorption of a layer of surface active chemical upon the hair fibre to give it good "handle."

According to Pickthall (14), the emulsified products of particular interest to the cosmetic chemist can be classified as follows:

(1) Lotions or milks : O/w emulsions–beauty creams, cleansing lotions, hair creams, etc.

(2) Pourable emulsions : W/o emulsions–hair creams.

(3) Creams : O/w emulsions–foundation creams, hand and cold creams.
W/o emulsions–emollients, skin foods, cold creams, etc.

In general, the oil phase may be considered the "active" phase whilst the water is present as a diluent or extender. Adsorption of the active ingredient by the skin or hair depends on several factors, and Blank (15) has summarized these as follows:—

(1) Relative solubilities of active material in the skin and vehicle phases.

(2) Concentration of active material in vehicle.

(3) Rates of diffusion in the phases.

(4) Chemical reactivity with constituents of the skin.

Before these factors can be effective, however, intimate contact between skin and vehicle must be achieved. Cationic surface active chemicals are able to aid the adsorption of active ingredients from emulsified products because of their surface adsorption. An emulsified system containing a strongly adsorbed hydrophobic emulsifier will become unstable when subjected to a large surface area as the emulsifier will be adsorbed, and so its concentration at the oil/water interface will be reduced. The adsorbed hydrophobic film will then be easily wetted by the oil phase, and the water will be displaced and can freely evaporate. The emulsifiers chosen for a product must be selected to produce an emulsion sufficiently stable to withstand normal handling and storage but capable of being "sensitized" on application.

### The Selection of Suitable Emulsifiers

Cationic surface active chemicals can be used to produce both o/w and w/o emulsions, but the w/o system favoured by surface active chemicals of low HLB value can be sensitized to a greater degree than o/w emulsions containing high HLB emulsifiers.

Approximate HLB values for some cationic emulsifiers are given in *Table IV* whilst *Table V* gives the required HLB values for emulsions of several common cosmetic materials.

Table IV
Approximate HLB values for cationic surface active chemicals

| Material | HLB |
|---|---|
| Polyethoxylated $C_{12}$ amine ( 5 mol ethylene oxide) | 13·0 |
| ,, $C_{12}$ ,, (15 ,, ,, ,, | 15·3 |
| ,, $C_{18}$ ,, (15 ,, ,, ,, | 16·7 |
| Didodecyl dimethyl ammonium chloride | 10·0 |
| Dodecyl trimethyl ammonium chloride | 15·0 |
| Cetyl ethyl morpholinium ethosulphate | 25–30 |

These figures illustrate the following generalizations on HLB values within a chemical series

(1) HLB value rises with increased ethoxylation.

(2) HLB value rises with increased chain length.

A further effect not illustrated here is the rise of HLB value with increasing degree of unsaturation of an alkyl chain.

Table V
Approximate HLB values required for emulsification (7,16)

| Material | HLB value | |
|---|---|---|
| | w/o emulsion | o/w emulsion |
| Stearic acid | 6 | 15–17 |
| Lanolin (USP anhyd) | 8 | 10–15 |
| Cottonseed oil | 5 | 7·5–10 |
| Heavy mineral oil | 4–5 | 10–12 |
| Light mineral oil | 4–5 | 10–12 |
| Petrolatum | 4–5 | 10–12 |
| Beeswax | 4 | 10–16 |
| Paraffin | 4 | 9–11 |

The pH of the system has a big influence on the properties of the cationic emulsifiers as at low pH values the cations are more strongly adsorbed than at higher values. The degree of surface sensitivity of an emulsion can be increased by

(a) using a less ethoxylated derivative,
(b) using a longer chain length derivative, and
(c) reducing the pH of the system.

## The Use of Cationic Surface Active Chemicals

Burton (17) has reported the spreading properties of a cationic emulsion formed with lanolin, cetyl alcohol, *iso*propyl myristate, and water (50%), with a quaternary ammonium compound as emulsifier. At 4.0% emulsifier, an o/w system was formed which did not invert on spreading or rewetting. At 0.4% the emulsion inverted on application to skin and reverted to o/w on rewetting, whilst at 0.04% emulsifier a w/o system resulted which did not change on application.

The selective wetting of the materials of construction of the emulsifying equipment have also shown to affect the type of emulsion produced. An emulsion system is quoted by Dvoretskaya (18) as giving an o/w emulsion using glass equipment whilst the use of a plastic agitator produced a w/o emulsion.

The lowering of the pH of an emulsion system using a quaternary ammonium compound can be achieved by using the fatty acid salt of the quaternary compound as reported by Hilfer (19).

$$\left[ R \cdot N\,(CH_3)_3 \right]^+ \quad Cl^- + \text{fatty acid} \rightarrow \text{Complex} + HCl$$

The adsorption of a quaternary ammonium compound onto fibres can be used to improve the "feel" of a blanket, and their bactericidal properties can also be used. An interesting product has been developed for treatment of hospital blankets (20) based on an oil emulsion using a quaternary ammonium compound

(a) as an emulsifier,
(b) as a sensitizing agent to give deposition of oil onto fibre, and
(c) as bactericide.

This type of formulation could be of value to the cosmetic chemist formulating deodorant and antiperspirant preparations.

The hydrophobic barrier of adsorbed quaternary can be utilized in hand and barrier creams as the quaternary ammonium compounds containing two long alkyl chains give water repellant films.

The reaction product of anionic and cationic surface active chemicals can also be of value, and a patent (21) refers to the use of such a compound as a water repellant carrier for therapeutically active substances.

Cationic surface active chemicals exhibit a high degree of substantivity towards keratin and the beneficial effects of an adsorbed layer on hair has been claimed in several patents (11-13, 22) and mentioned elsewhere (23,24). Cationic chemicals have been used as solubilizing agents for certain dyestuffs giving products having high substantivity and dye levelling properties.

Emulsions are often desirable for aerosol formulations, particularly those designed for cosmetic use. The results of a study of a wide range of surface active chemicals showed that all classes have members which give good emulsifying and foaming characteristics. Of the cationic materials investigated the difatty quaternaries, e.g. distearyl dimethyl ammonium chloride, gave results similar to an alcohol sulphate, a sodium sulphosuccinate di-ester and a sorbitan ester. The effect of various additives on the propellant water systems were also studied and it was found that the emulsions were very stable, and not sensitive to other ingredients likely to be found in cosmetic formulations.

A polyethoxylated laurylamine having 5 mol of ethylene oxide was found by Lesshafft and De Kay (25) to give optimum release of mercuric oxide and iodine medicaments when used at 1% in place of sodium lauryl sulphate in the standard formulation in USPXIV. Increase in the surface active chemical concentration causes a decrease in release which emphasizes the necessity to formulate to optimal levels as over-usage can annul the beneficial effects of these systems.

Several papers and patents (26-30) refer to the use of cationic surface active agents in cosmetic products, and reference to them will indicate some further ways of making use of the properties of these interesting chemicals.

## REFERENCES

(1) Du Brow, P. L. *Am. Perfumer Aromat.* **72** 95 (October 1958).
(2) Lawrence, C. A. *Soap Perfumery Cosmetics* **27** 369 (1954).
(3) Hilfer, H. *Drug Cosmetic Ind.* **76** 466 (1955).
(4) Addison, C. C. and Furmidge, C. G. L. *J. Sci. Food Agr.* **5** 212 (1954).
(5) Shibe, W. J. and Hanson, D. H. *Soap Chem. Specialties* **39** 83 (1964).
(6) Seyforth and Morgan, *Am. Dyestuffs Reptr.* **27** (19 September 1938).
(7) Griffin, W. C. *J. Soc. Cosmetic Chemists* **1** 311 (1949).
(8) Griffin, W. C. *ibid* **5** 249 (1954).
(9) Tamamushi and Tomaki, *Proc. 2nd Intern. Congr. Surface Activity* **III** 449 (1957).
(10) Lincoln, P. A. *J. Soc. Cosmetic Chemists* **8** 222 (1957).

(11) U.S. Pat. 2,930,761
(12) Brit. Pat. 867,874
(13) Brit. Pat. 823,303
(14) Pickthall, J. *Perfumery Essent. Oil Record* **51** 299 (1960).
(15) Blank, I. H. *J. Occupational Med.* **2** 6 (1960).
(16) Carter, P. J. *Am. Perfumer Aromat.* **71** 43 (June 1958).
(17) Burton, D. N. *Mfg. Chemist* **22** 267 (1951).
(18) Dvoretskaya, R. M. *Kolloidn. Zh.* **13** 432 (1951).
(19) Hilfer, H. *Drug Cosmetic Ind.* **65** 394 (1949).
(20) Cardew, C. V. *Soap Perfumery Cosmetics* **24** 154–7 (1951).
(21) Brit. Pat. 767,840
(22) Brit. Pat. 891,600
(23) Hilfer, H. *Drug Cosmetic Ind.* **68** 322 (1951).
(24) Mills, C. M., Ester, V. C. and Henkin, H. *J. Soc. Cosmetic Chemists* **7** 466 (1956).
(25) Lesshafft, C. T. S. and de Kay, H. G. *Drug Std.* **25** 45 (1957).
(26) Sagarin, E. Cosmetics : (1957) Interscience, New York.
(27) Brit. Pat. 641,203
(28) U.S. Pat. 2,543,061
(29) Lincoln, P. A. *Chem. Prod.* **17** 407 (1954).
(30) Brit. Pat. 699,752

## DISCUSSION

MR. D. E. HERRING: Could you give any indication of how the HLB values in *Table IV* were obtained? Are they in fact theoretical or determined figures?

THE LECTURER: The HLB values given in *Table IV* are, I believe, practical ones. I have not determined them myself. I think they would be obtained by a substitution method. The theoretical values are slightly different from those given. For the C-12, 5 mol ethoxylated amine the theoretical value would be 11.0. For the C-12, 15 mol ethoxylate derivative, 15.7, and for the C-18, 15 mol derivative, 14.3. One would expect this decrease between the C-12 and C-18 derivatives of equal degrees of ethoxylation as the overall molecular weight increases for the same number of mols in ethylene oxide.

MR. D. E. HERRING: Since amines, and particularly ethoxylated amines, form salts in acid solution, one would anticipate the HLB value to vary with pH. Would you care to comment on this, and would you care to say whether there is a sharp change or a gradual one?

THE LECTURER: The HLB value must be considered for the system as a whole so that the amine salts will have a higher HLB than the basic materials. I have never seen any results relating pH to HLB so I just do not know whether the change is gradual or stepwise.

MR. W. D. MACMILLAN: I would like to refer to *Table II* in which some very useful information is given concerning the variations in surface tension and wetting times in relation to the number of ethylene oxide molecules per mol of amine. I wonder, however, if you have any further information concerning the sensitization of the skin by these compounds and whether this varies according to the HLB of the ethoxylated amine.

THE LECTURER: I can make the generalization that sensitization decreases with ethoxylation, i.e. it decreases with increased HLB. The nearer one is to the basic amines the higher the sensitization. There is a very great increase between the amine and the 2 mol ethoxylate, i.e. from the primary to the tertiary amine; the sensitizing effect of the tertiary amine is very much reduced compared to the primary amine. The chain length also has an effect and the lower fatty derivatives have a higher sensitizing effect than the longer chain materials.

MR. C. PARRY: In *Table I* the reputed phenol coefficients for the quaternary ammonium compounds are given. I agree that the gram-positive organisms such as *staphylococcus* are more susceptible to the quarternary ammonium compounds, but the use of phenol coefficients for these quaternary ammonium compounds has been shown to be meaningless in these cases. This is indicated by the fact that British Standards Specification 3286, which is used for the evaluation of the quaternary ammonium compounds, specifies that the Rideal Walker coefficients should, in fact, be used solely for phenolic derivatives. Have you any further comments on this?

THE LECTURER: Apart from accepting your comment in the spirit in which it is given, the figures here are given purely as a guide, and I have tried to emphasize how meaningless figures of this type can be. Apart from the method of evaluation, it is a fact that any formulated product must be considered as a whole and no results for any one component can be accepted as such. I agree that the R.W. figures in themselves do not mean a great deal in today's thinking, but they do at least allow us to form some sort of comparison between one compound and another. They are not absolute values.

MR. R. F. L. THOMAS: A number of papers have recently been written on the inactivation of germicides in conjunction with nonionic emulsifiers. Have you any experience of this, and do you feel that in relation to cationics there is a drop in bactericidal activity in the presence of the majority of nonionic emulsifiers?

THE LECTURER: I think there is. If one considers the action of a quaternary to be adsorption on to the bacteria surface, it is reasonable to expect that in the presence of a nonionic the adsorption equilibrium would move towards the aqueous phase and the concentration at the surface would be reduced. In the presence of nonionics the position of the equilibrium must therefore shift away from adsorption and hence affect the efficiency of the materials as bacteriocides.

MR. R. L. STEVENS: Could you please expand a little more on the subject of w/o emulsions manufactured with quaternary ammonium compounds? Perhaps some of the references which you cite give further information.

THE LECTURER: I would suggest (17) and (23). In general, the HLB value must be reduced and the materials of particular interest are the difatty quaternaries, and the ethoxylated difatty quaternaries. Long chain fatty derivatives with a small degree of ethoxylation, or short chain difatty quaternaries are materials of particular value.

DR. B. A. SCOTT: Is the deposition of oil on substrate dependent on the concentration of cationic? For example, do you see a bimolecular film which is positively charged at high concentrations of cationics? Does the oil deposit on the substrate in these circumstances or is it affected by electrostatic repulsion?

THE LECTURER: One can build up double layers and the quantity of material is fairly critical. On most plain surfaces the amount of material required to build up this level is very small, and so the amount of surface sensitive emulsifier used must be kept very low. The rate of deposition will be affected by the level of use but deposition will still occur at a high level of surface active material. The mechanism could then be related to degree of hydration rather than to electrostatic forces.

*J. Soc. Cosmetic Chemists* **17** 29-44 (1966)

# Some principles and difficulties of topical treatment in dermatology

G. HODGSON*

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

**Synopsis**—The majority of dermatological topical treatment is used for alleviation of symptoms. These arise from systemic disease, or are just temporary, or longer lasting, individual variations in functions of the skin from the physiological mean. The efficacy of established topical treatments is discussed, including the use of anti-perspirants and detergent acne preparations.

Antipruritic agents usually act by anaesthetizing pain fibres or reducing bacterial degradation of protein to polypeptides, which provoke itching. Both local procaine-type anaesthetics and antibiotics, especially the 'mycin' group, are liable to cause sensitization.

Topical steroids used under occlusive polythene dressings to increase hydration and permeability in established eczema or psoriasis may cause severe local degeneration of collagen with epidermal thinning, skin stretching ('striae') and bruising, in addition to systemic absorption effects.

The treatment of melanosis with bleaching agents, or hydroquinone monobenzyl ether, is clinically and cosmetically unsatisfactory, as is that of depigmentation with methoxy psoralens or disguising agents as dihydroxy acetone.

## THE CHANGING FACE OF DERMATOLOGY

The practice of dermatology does not depend as much as formerly upon topical applications. Those days were without antibiotics, antihistamines, steroids, and other agents to be effectively administered systemically. These older medicaments were both complex and simple ; complex because of the polypharmacy of the ingredients, of which few chemists will mourn the passing, and simple because the vehicles had not yet seen the transformation to the more pleasant and effective emulsified and water-washable applications for which we owe so much to the cosmetic industry.

---

*Lecturer in Dermatology, Welsh National School of Medicine, Cardiff.

Unnas' shake lotions are ageless and still used but calamine lotion, like Cinderella, is now transformed under the magic wand of cosmetic emulsifier and colloid mystique, technically described by Wells and Lubowe (1), to parade unrecognized in many creams, liquid face powders, compacts and other make-up preparations of the beauty parlour.

New topical applications, however, have not solved many of the problems of treatment and some have brought new difficulties.

Discussion of some of these, with cosmetic chemists and a clinical dermatologist meeting on common ground, may be mutually helpful.

## THE CHANGING SKIN

Generally speaking, except for common skin diseases such as bacterial infections, infestations, contact dermatitis, etc., most topical treatment is used to remove or ameliorate a symptom.

This symptom can be an expression of a systemic illness, but more often it is just a temporary functional variation from the physiological mean, as in epidermal keratinization and dermal functions involving sweat and sebaceous glands (including acne and seborrhoeic conditions), pigment formation, vascular activity including, for instance, frictional urticaria (dermographism), hypersensitive reactions to cold ("white fingers", chilblains), and other individual responses to radiant energy and the environment.

These normal variations in personal physiological function or reaction to environment only require treatment when such factors produce temporary symptoms.

A grosser disturbance of function from the mean may cause a symptomatic but still only temporary state of inflammation from which recovery soon or gradually occurs. In those in whom the skin is genetically predisposed to be "an inferior organ" epidermal functions such as keratinization, or dermal functions such as sweating, or others may be so disturbed that the skin recovers only slowly, if ever, as in chronic eczema and established psoriasis. These patients may require continued symptomatic emollient and anti-inflammatory treatment. Greater emphasis should be placed on the prophylactic treatment of these constitutionally inferior skins before such chronic functional disturbance occurs. The problem is more complex because in all persons the physiological or enzymic function, biochemistry and often the anatomy varies considerably from area to area. As illustrations, skin grafted from the thigh to the forehead always remains as thigh-type skin in its new position ; the cycle of hair growth varies ;

itch sensitivity varies ; moles and papillomas become tag-like or pedunculated on such areas of skin as the eyelids, neck (as seen in menopausal women), groins and axillae simply because, in some way, the skin is different there. Absorption of medicaments is also much influenced by the thickness of the horny layer as on the palms or soles compared to thin facial or flexural skin. The fundamental biochemical and enzymic differences, however, have still largely to be determined.

## Disorders of Keratinization

The integrity of the main epidermal barrier (the stratum corneum) depends mainly upon the intact linear protein (keratin) chains and their firm cross-linking by the strong disulphide (cystine) and weaker hydrogen and salt links of individual amino acids. The protein manufacture in the lower viable epidermal cells, and the degradation in the outer dead horny layer is enzymically determined. The integrity, however, also depends upon an adequate water content replaced from sweat in and between the keratin chains to keep the skin supple, in turn protected by a layer of oily sebum which prevents evaporation.

Patients with inherent abnormalities of keratinization, and varying capacity to retain water, are particularly liable to functional disturbance from physiological, environmental or disease factors. They may be seen as a spectrum from severe types of ichthyosis, the harlequin foetus whose skin is incompatible with life, through grades of ichthyosis to the milder forms as seen in most atopics (subjects of the eczema-asthma-hay fever-syndrome) and senile skins, to mild skin xerosis and keratosis pilaris where the defect is seen like a nutmeg grater at hair follicles of the arms and legs. The group to be treated also includes dry states of the skin convalescent from inflammations such as eczema. These skins make up a large community who often require topical symptomatic therapy.

## The Hydration of Keratin

Reduction of water content by evaporation or climatic conditions when a cold dry spell causes a rise of barometric pressure and dew point (where gaseous moisture condenses) produces dryness, chapping, and stiffening of the keratinous horny layer in these susceptible skins.

In the background parade many minor disorders. Among these are the superficial dry flaky eczemas of the face, *pityriasis alba* (the "tetters") as in children, chapping of wrists or hands especially where wet work increases evaporation, as in housewives or behind the knees in children, and dry, chapped lips in mouth breathers, unconscious persons, or those who continually lick their lips as a nervous habit.

Splits may occur in thin and brittle skin behind the ears, or sides of the mouth or vestibule of the nose in those who habitually blow the nose with vigour ; secondary growth of bacteria in these sites are continual sources of cutaneous infection in the neighbourhood, as occurs with boils.

Nail affections include fissuring of the nail cuticles or "hang nails" with secondary nail fold infections, and brittleness of nails ; similar but more pronounced nail changes with tenderness, discolouration and the collecting of warty keratinous debris has occurred through occlusive disturbance of hydration with artificial finger nails.

Solvents used for hand cleaning in industry allow dehydration through the removal of the waterproofing sebum, as also do alkaline agents and washing powders.

## SUSCEPTIBILITY TO IRRITANTS

Abnormally keratinized or dehydrated skin is also susceptible to mechanical trauma and to frictional and chemical irritants because of its inelastic state, and because of the ease of damage to the keratin molecule.

Weak chemical irritants of everyday life, such as alkalis in washing agents or cement and reducing bleaching agents, easily disrupt the strong disulphide molecular chain links in dry skins, in the same way that oxidizing agents will effect the weaker hydrogen links.

Later penetration of chemicals or bacteria are then able to provoke allergic or persisting eczema reactions, the patient presented with a chronic relapsing patchy eczema.

Other examples of these effects are winter eczema on the outside of the legs of those who over-bath, are soap intolerant and who wear heavier clothing in the winter ; the asteatotic eczema of the man who is over-scrupulously clean and is constantly washing his hands ; the squamous eczemas of the palms in those using hand tools in industry ; and the chronic patchy industrial eczema of those constantly exposed to weak irritants, alkaline materials, oils, solvents, or wet work.

The frictional effects of wearing apparel are also increased, as are degrees of itching by dry spicules of projecting keratin and abnormal irritability of the erector pili muscles with cold or nervous tension which causes a more prominent elevation of the hair and follicle. Static electricity generated by nylon or *Terylene* fabrics can also cause discomfort in these persons. These subjects also find the prickly effect of wool fibres uncomfortable, or liable to cause eczema reactions.

## Sweat Difficulties

A considerable number of those with constitutionally dry skins will admit that they have never perspired easily or freely.

Microtrauma on the skin will first show itself in a hyperkeratotic closure of the sweat duct (2) with obstructive dilatation of the duct, and interruption of sweat replacement of water to the keratin.

Prickly heat eruptions (miliaria) in these dry-skinned persons are common in hot climates or environments, especially where clothes provoke a frictional microtrauma. Papular miliaria and eczema reactions thus occur in colliery workers where belt, lamp battery or cap hands minimally traumatize the skin, or in women wearing tight or rubberized foundation garments.

The common and distressing symptom of anal irritation (pruritus ani) in non-sweating subjects also appears much influenced by sweat obstruction. Persisting obstruction to sweat pores commonly leads to relapses in the form of papular eczemas of the body, or vesicular pompholyx eczema of the hands in those convalescent from contact dermatitis or eczema. Astringent face lotions, excessive sun burn, excessive use of Turkish baths may also provoke such symptoms, at a later date.

## Itching (pruritus)

The itching sensation is produced by subliminal stimulation of pain fibres, and can be abolished by conversion to pain. The qualities of itching are sharp, needling pricks or more diffuse burning sensations. Agents cause itching either mechanically or by releasing polypeptides from degraded protein produced by inflammation, enzymic effects of bacteria or other factors on the pain fibres. "School boy" itching powder from the plant *Mucuna pruriens* irritates mechanically, and by its polypeptide nature. Slight itching is physiologically normal in the skin due to such factors as friction of clothes, enzymic protein breakdown, bacterial growth, sweating, circulatory and temperature changes, although much personal and site differences exist in individuals. Dry skins are often more itchy presumably through minor inflammations, sweat obstruction and abnormally keratinized scales catching on clothes.

## Efficacy of Topical Treatment

### *Sedative and emollient medicaments*

Most generally used for slight keratin disorders is hydrous ointment, Ung. Aquosum, B.P.–w/o emulsion with wool alcohols ointment. It is effective as a hydrating agent but very greasy and less cosmetically pleasant than many proprietary w/o emulsions of liquid paraffin, soft paraffin, adeps lanae and emulsifying agents specially formulated for dry skins.

Dry, chapped hands and brittle nails respond well, especially when the cream is used overnight under occlusive polythene gloves which increase hydration through reabsorbed perspiration. Chapped lips are less satisfactorily treated although emulsion creams with silicones help to lessen water evaporation. Self-emulsifying bath oils should find increasing use for senile skins and dyskeratotic skins in adverse climates. The oils seem well absorbed by abnormal keratinized skin, mineral oils adhere better than vegetable oils absorption being increased by temperature and duration of immersion (3). Some atopic eczema subjects are more comfortable if they bath twice a day in colder, dry weather.

More severe degrees of ichthyosis are usually less satisfactorily treated by routine baths followed immediately by emollient greasy creams such as hydrous wool fat ointment, ung. adeps lanae hydrous containing hydrous wool fat and yellow soft paraffin, or wool alcohol ointments B.P. (wool alcohol 6% with hard, soft and liquid paraffins), or white petroleum jelly. Sodium chloride 10% has been used in petroleum jelly to increase water holding capacity but some development of preparations along the lines of cosmetics with humectants which can be prescribed under a national formulary would be welcome.

### *Cleansing agents and barrier creams*

Intolerance of soapy detergent cleansing agent is often on a personal basis due to alkali intolerance or penetration of fatty acids, more likely through non-intact keratin.

Industrial barrier creams are now *sub judice* until controlled industrial trials under actual working conditions support or disprove the makers' claims. Most agree that the complete protective "invisible glove" is impossible to attain or maintain under normal working conditions, but that they are not entirely useless. They do not on their own prevent dermatitis, nor stop the entrance of sensitizing chemicals, and are only to be considered as a part of the general prevention programme. They are not helpful with such common irritants as cement, oils or continuous exposure to wet conditions.

Vanishing creams and hydrophilic water-miscible creams help in hand-cleansing, but the soap content may be deleterious to alkali-intolerant and dry skins.

Neutral soapy or non-soapy synthetic detergent barsrecently introduced as cleansing agents have been most helpful in alkali-sensitive persons. Similar difficulties arise in management of facial acne where excessive washing with soap on dry skin is not tolerated on the peripheral non-acne bearing areas of the skin, although the central acne areas require this. On the scalp, the removal of desquamated keratin as dandruff and scales by anionic and nonionic soapless shampoos has greatly facilitated head cleansing and ointment removal but difficulties have arisen with some shampoos containing alkyl benzene sulphonates and selenium which may actually increase oily seborrhoea and scalp greasiness (4).

### *Anti-itching agents*

Cooling produces effective relief of itching, hence the temporary relief from evaporating lotions, simple w/o emollients or agents, e.g. menthol producing a cold sensation. Low sensitizing antibacterial or antibiotic agents which reduce the enzymic degradation of protein are usually effective when combined with hydrocortisone in the relief of pruritus ani, scalp itching or developed eczema although the effect of the application may not last sufficiently long.

Many antipruritic agents can only act by anaesthetizing the nerve endings, and having thus to penetrate through non-intact skin they can irritate or sensitize. Predominant among these are the local anaesthetic procaine-type ointments and the antihistamines, especially pyribenzamine ; both are very common sensitizers.

Phenol and other coal tar distillates are much less likely to irritate though a few are intolerant.

### *Anti-infective agents*

A vast, post-war literature has been collected on the sensitization potential of chemotherapeutic agents (sulphonamides) or antibiotics (penicillin, etc.) Of increasing importance is neomycin with an ability to cross-sensitize with such other "mycins" as kanamycin, soframycin, framycetin, and bacitracin. Less likely to sensitize or irritate are quaternary ammonium salts and hydroxyquinoline derivates, but cross-sensitization exists between the members of this last family.

### *Anti-inflammatory agents*

Topical hydrocortisone and fluorinated steroids have transformed the general management of eczema and of psoriasis, that inherited defect in keratinization, but their extreme activity and ability to penetrate, increased by emulsifying agents, has introduced difficulties.

The occlusive treatment both of chronic eczema and psoriasis by topical steroids under polythene leads to increased hydration and permeability of the skin, and considerable penetration of the steroid through the wet skin. Absorption can occur even without polythene in areas of skin like the groins, axillae or eyelids ; glaucoma may be a risk.

The chief disadvantages of this most effective treatment are prickly-heat sweat retention rashes, offensiveness and skin sepsis from bacterial growth, increased risk of irritant or sensitization effects from incorporated anti-infective agents, and injury from absorption of the steroid. The latter causes a temporary blanching when absorbed (*Fig. 1*), but continuous absorption can cause degeneration of the skin with stretching "striae," easy or spontaneous bruising and epidermal thinning (*Fig. 2*). The skin exhibits local transparency from collagen degeneration. Systemic absorption may cause a similar collagen degeneration on other non-contact areas of the skin, in addition to the systemic effects which occur with steroid therapy in general.

## DISORDERS OF SWEAT AND SEBACEOUS GLANDS

Hyperidrosis of axillae is satisfactorily managed by non-irritant concentrations of aluminium salts, e.g. aluminium chlorhydroxide. Less satisfactory is the management of sweating on hands and feet in adolescence, or in those handling steel in industry, who are termed "rusters."

Formalin is often a sensitizer and 10% sodium hexa-*m*-phosphate or dusting powders with mild poral irritants (tannic and salicylic acids) are not effective for long. The problem is difficult as nervous emotional factors so often operate, and those with defective sweating on the body often sweat more on these areas ; the use of systemic ganglion blocking agents may upset temperature regulation.

*Acne vulgaris* well exemplifies the normal physiological and anatomical variations of the adolescent or young skin from the stimulus of androgens ; the total course usually determined by personal susceptibility until its self-determined end. Though bacterial infection aggravates, essentially the problem of management in the young is the lessening of the mechanical obstruction of the follicle opening caused by the sebum and follicular

*Figure 1*

Psoriasis with surrounding blanching and atrophy from topical steroid.

*Figure 2*

Systemic absorption. Atrophic striae after topical steroids.

*Figure 3*

Periocular melanosis due to perfumed face cream.

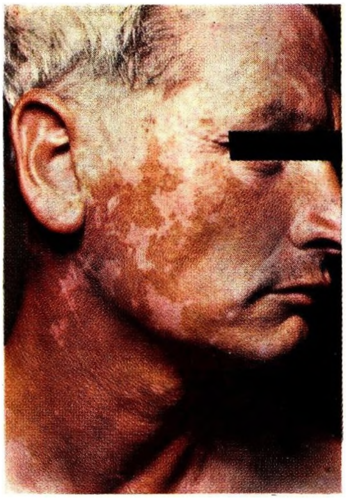


*Figure 4*

Idiopathic vitiligo.

hyperkeratosis to allow free exit of secretion. Similar problems exist in those who develop industrial acne from oil, tar and pitch hydrocarbons. The introduction of anionic and other detergent cleansing agents combined with antibacterial agents has improved matters but often this is still unsatisfactory and temporary, and patients get tired of routine treatments. The provision of further cleansing and fat-emulsifying agents would help these subjects.

## PIGMENTATION AND DEPIGMENTATION

The oxidation of tyrosine by the enzyme tyrosinase copper-catalysed to dopa (1′3,4, dihydroxyphenylalanine) and thence to dopa quinone and 5,6 dihydroxy indole to reduced (tan) or oxidized (black) melanin is inhibited by sulphydryl groups. It seems, however, that the normal epidermis itself may also control melanogenesis. Both water-soluble and insoluble extracts of human skin prolong the formation of dopa quinone, though not beyond this stage (5).

Excluding hormonal influences through the adrenal, pituitary, thyroid glands or gonads in normal life, excessive melanosis is usually produced by radiant energy (mainly UV light) duly increased by photosensitization. Among agents which photosensitize or increase the absorption of light are bergaptens and psoralens in umbelliferae plants (parsnips, carrots, cow parsley) or citrus fruits (oil of bergamot), perfumes in cosmetics (*Fig. 3*), soaps, and drugs, e.g. the phenothiazines. Similarly, coal tar, pitch hydrocarbons or petroleum lubricating and cutting oils cause melanosis as an occupational hazard. It can, however, also occur from direct chemical or traumatic irritation of the skin, or from infections which reduce the sulphydryl groups and release the inhibition of tyrosinase. Depigmentations may be congenital and genetically determined as in albinism or acquired in vitiligo or leucoderma (*Fig. 4*); the latter may follow defective hormone production or local eczematous and other inflammation in the skin.

Agents such as hydroquinine benzyl ether (*Agerite alba*) used as antioxidant in rubber manufacture also cause depigmentation of workers' skin either by some antienzyme effect or by its dermatitis-producing effect (6). In idiopathic vitiligo, melanin is not produced in melanocytes but spontaneous recovery can occur. Negro skins are particularly liable to depigment which may lead to unfortunate results in cosmetic surgery. Treatment of disfiguring melanosis is most unsatisfactory ; either when produced by hormonal causes but more often from such photosensitizing ingredients in cosmetics or soaps as perfume, hexachlorophene (7), bithionol, or halogenated salicyl anilides.

Suntan preparations will reduce the absorption spectra of light rays and change them into tanning rays. Pyribenzamine and monoglyceryl *p*amino benzoates will cause contact sensitization. Large doses of ascorbic acid can reduce oxidized dark melanin to the reduced form (8), and prevent the later oxidation to dopa quinone. Hydroquinone monobenzyl ether mainly depigments after it has produced contact dermatitis, but its effects are most variable and patchy ; cross-sensitization occurs with other common quinone sensitizers, e.g. *p*phenylenediamine, and with azo dyes, as in foods, petrol or textiles.

Bleaching agents (mercurials) as used in freckle creams which probably displace copper and interfere with tyrosinase, are often irritant and sensitizing. Possibly some future approach could be made through an active agent which would inhibit the enzyme without denaturing its protein.

Treatment of depigmentation is equally unsatisfactory ; the efficacy of the photosensitizing agent 8-methoxypsoralen in increasing pigmentation is doubted in the controlled experiment of Cahn *et al* (9) who found no erythema or pigmentation histologically after exposure.

Staining agents used include potassium permanganate or fresh walnut stain, and lately, dihydroxyacetone D.H.A. (1,3, dihydroxy-2-propanone) in a 2.5% alcoholic lotion (10). In combination with keratin this may, however, cause contact dermatitis (11). Conversely, removal of keratin stains in industry is a problem. None of these seem to give a normal skin colour and further research is needed for some suitable dye in which the shades can be more easily varied to suit the individual.

(*Received : 21st December 1964*)

## REFERENCES

(1) Wells, F. V. and Lubowe, I. I. *Cosmetics and the skin* (1964) (Reinhold, New York).

(2) O'Brien, J. P. *Brit. J. Dermatol.* **59** 125–158 (1947).

(3) Knox, J. M. and Ogura, X. X. *Brit. Med. J.* **2** 1048 (1964).

(4) Skog, E. *Acta Dermato-Venereol.* **38** 15–19 (1958).

(5) Findlay, G. H. *S. African J. Lab. Clin. Med.* **8** 26–30 (March 1962).

(6) Lorincz, L. A. in Rothman, S. *Physiology and Biochemistry of skin* Chap. 22 (1953) (University Press, Chicago).

(7) Newcomer, V. D., Lindberg, M. C. and Sternberg, T. H. *Arch. Dermatol.* **83** 284 (1947).

(8) Rothman, S. *Proc. Soc. Exp. Biol. Med.* **45** 52–54 (1940).

(9) Cahn, M. M., Levy, E. J. and Schaffer, B. *J. Invest. Dermatol.* **36** 193–198 (1961).

(10) Mumford, P. B. *Brit. J. Dermatol.* **72** 279 (1961).

(11) Harman, R. R. M. *Trans. St. John's Hosp. Dermatol. Soc. London* **47** 157 (1961).

### *Introduction by the lecturer*

I would like to stress that I am a practising dermatologist, without any pretensions to being an expert in cosmetics or their chemistry. However, I thought that it would be interesting to discuss some of the problems that confront us in day-to-day practice. Many of the minor complaints are just a nuisance and are not real illnesses of the skin; they represent changes in the normal skin physiology from day to day and even from hour to hour. For instance, urticaria or nettlerash is almost normal; it is an immune reaction in the skin. We all get urticaria, but there are some people in whom it becomes chronic, like a "bad habit," and once initiated, it goes on and on. It is then extremely difficult to arrest, as so many factors can have a causative influence.

A large group of people we have to treat are those who have defective or inferior skins, for they suffer from defects in keratinization. This is a difficult problem, for we are only now beginning to realize that the skin is not the same over all parts of the body. For example, the deposition of fatty material in the eyelids of some people, known as xantholasma, is due to a local accumulation of cholesterol and related substances. We have to ask ourselves why it occurs there and not everywhere else. There is evidently something different about these areas of skin. I recently saw a patient who was pregnant and who presented an extraordinary picture; down one arm only she had literally hundreds of angiomata, or small, visible blood vessels. This condition was obviously hormone-induced but why did the hormones not stimulate such blood vessels to hypertrophy all over her skin? In another parallel case, all the angiomata disappeared when the baby was born. This area of skin is evidently susceptible to some hormonal influence unlike the rest of the skin.

I suppose it is fair to say that the protection of the skin depends mainly on the dead horny cells being fully keratinized, secondly on the water content which keeps it supple, and thirdly upon the sebum which seals in this water and retards evaporation. The degrees of abnormal keratinization range from very severe to very mild types and it is the mildest types that we mainly have to treat. A large number of people have a mild type of imperfectly keratinized dry skin or xerosis. Do you consider making cosmetics especially for such people or cosmetics for various other types of skin, or even for different areas of the skin?

I should next like to consider some of the more abnormally keratinized skins. We had an example of gross ichthyosis where there were areas of heaped-up keratinous horny material on a man's back, literally an inch deep. We have improved him a good deal simply by applying hydrous ointment under polythene. The horny material peeled off, and although he has considerably improved, it will regrow; yet this does show that much can be done just by replacing the water content in the skin.

In the case of mild ichthyosis, many people have a mild xerosis of the legs although the rest of the skin appears quite normal. The skin on the face may be greasy; but chapping affects the legs and especially the heel, particularly in the winter. Sometimes a minor degree of ichthyosis affects the hair follicles; we describe this as being like a nutmeg grater or keratosis pilaris.

Another group of abnormally keratinized, dry skins is the atopic, i.e. people with the eczema-asthma-hay fever syndrome. They are not more allergic than their fellows to external agents causing eczema or contact dermatitis, but they do have an inborn allergy to foreign proteins which yield this syndrome. They probably develop eczema because they have an inferior dry skin which is easily damaged. In atopic eczema, the flexural thickened skin is very itchy and troublesome.

These people with abnormal skins suffer various disabilities. The first thing is reduction of the water content, leading to numerous minor disorders for which treatment is sought. For example, they may well have winter chapping of the hands. Another condition, mostly seen in children, is a dry, flaky eczema of the face during winter known as pityriasis alba, which clears up in the following summer; it may leave white patches on the skin as the excessive moisture prevents solar pigmentation.

Then there may be chapping of the lips, particularly in people who have any obstruction of the nose or large tonsils or adenoids so that they breathe through the mouth. These cracked and chapped lips may lead eventually to chronic eczema. We help them by trying to hydrate the keratin again and by lessening evaporation, through putting on silicones overnight. Some of these people have a habit of licking the lips and they can develop a chronic cheilitis. Chronic fissuring either side of the mouth follows the same principles. The skin is always wet in this area and as it dries, the skin loses its elasticity and cracks. This is more common with ill-fitting dentures but it often affects the atopic, dry-skinned person.

Dry skin behind the ears is also liable to crack easily. This is a problem from the standpoint of infection. Most people carry organisms on the skin without ill-effect, but patients with eczema and acne are subject to repeated infections perhaps because they carry staphylococci in fissures or the nasal vestibule. Sepsis may occur behind the ears, in the nose, on the face or as boils on the trunk, in the groins or in any area of eczema.

Many people are susceptible to solvents used for cleaning the hands, since these defat and dehydrate the skin. They are also susceptible to physical trauma. Contact dermatitis usually involves all the areas in contact, and bacteria also commonly produce a sensitization eczema. The starting-point may well be friction with clothing, or hot bathing with alkaline soaps which open the way for penetration of bacteria and chemical sensitizers. Dry-skinned persons also have problems in industry. As the skin has diminished flexibility, a squamous eczema may develop on areas of pressure; this is commonest in the 40–50 age group, when endocrine involutional changes are taking place. This type of eczema is especially difficult to treat successfully as the patient has to go on working.

Another problem of the dry-skinned person may appear as difficulty in sweating freely. Microtrauma to the skin cause keratinous obstruction in the sweat pores, leading to various gradations of miliaria or "prickly heat." Such eruptions are extremely common; I am sure that many people who complain of trouble with cosmetics do not suffer from a true contact dermatitis at all, but from a poral obstruction due to friction or excessive sweating.

Sweat obstruction also occurs on the hands in people wearing protective gloves for long periods of time and in emotionally unstable people who sweat a great deal. They develop a hand eczema termed pompholyx, cheiropompholyx or dyshidrosis. Mechanical obstruction to sweating is a common eczematous reaction which relapses easily. In the unusual event of a cosmetic contact dermatitis, a second episode is often caused by a pre-existing sweat obstruction due to previous inflammation or to the treatment given; as soon as the patient gets hot, the eruption starts again. I have seen this in people holidaying in unfamiliar climates such as Italy, where they become excessively sunburned. On returning home, a miliaria may follow.

A dry skin itches very commonly because of the minor inflammations or from sweat obstruction which gives a prickling sensation. Many people notice that they start prickling all over when getting into bed. This is quite common in active eczema or in abnormal dry skins. Bacteria breaking down protein will cause itchiness, but minor itching is a universal symptom which may easily be produced by a variety of causative mechanisms.

As to treatment, we deal with most of the dry skins by trying to replace the water content with emollient ointments. Conditions like cracked hands or brittle nails can do very well with polythene gloves and a hydrous ointment. Such gloves may, however, lead to a sweat obstruction syndrome with prickly heat or a dyshidrotic eczema. The more severe degrees of ichthyosis are difficult to manage and we would really like some help in providing a satisfactory preparation which would be continuously emollient and keep the patients comfortable. Anti-itching agents are mainly designed to cool the skin – cooling being an effective way of reducing irritation – to lessen the dryness or to have an antibacterial effect on organisms that degrade proteins into polypeptides causing itchiness. Many of these antibacterials and the antipruritics which act on the sensory system are, however, sensitizing agents.

Abnormal skins often recover completely to their original, slightly abnormal state after slight irritations, but if the skin is sufficiently damaged it seems to develop the "bad habit" of producing the eruption again and again. In this category falls the individual who becomes more and more sensitized to the topical applications applied for the treatment of a skin condition. If the areas of imperfectly keratinized skin are removed in psoriasis, the skin almost returns to normal although it can never be completely normal. If areas of psoriasis are left untreated, there is a tendency to produce further psoriasis; the longer the patient has it, the more chronic it becomes and the skin is more liable to develop the habit of producing it.

The anti-inflammatory steroids first introduced for the treatment of psoriasis proved extremely effective, but as they became more potent, they began to cause trouble. We had already found that giving steroids internally to patients would suppress the psoriasis, but as soon as one withdrew the steroid, the psoriasis rebounded and was then more difficult to control. This is also a real difficulty with topical steroids; sometimes the skin becomes so unstable that it produces psoriasis as a result of almost any stimulus and the psoriatic reaction may change qualitatively. The topical steroids are easily absorbed and they can produce quite marked collagen degeneration locally with thinning of the skin. The whole skin becomes more transparent, with the venules and capillaries showing through. Not only may there be a local degeneration but absorption and systemic degeneration may follow elsewhere giving rise to striae, for example, either at the site of application or in a remote site.

Acne is a condition representing just a physiological variation in the normal skin. I feel that many of the present day treatments are not very satisfactory. Bacterial infection probably plays a major part in producing the gross scarring and inflammatory lesions, but basically the problem is one of cleaning the skin and of removing the sebum and keratin plugging the sebaceous orifices. This is illustrated by cutting oil folliculitis, also known as "oil acne," due to contact with an engineers' cutting oil which results in obstruction of the hair follicles. These people require help by providing them with a cleansing agent which will emulsify the collection of petroleum oil and sebum in the pilosebaceous orifices. A very large percentage of workers on multiple cutting machines may be afflicted.

While it is normal for every one to become pigmented, individual responses vary. Excessive pigmentation may represent photosensitivity due to certain perfume constituents, as in the case of bergamot oil. Hyperpigmentation is often difficult to diagnose and also to treat, since we are not certain of the causative agent to be avoided. In my experience, the treatment of melanotic pigmentation is unsatisfactory at the moment even when using hydroquinone benzyl ether. Equally difficult is the treatment of depigmented skin; the process of demelanization is not yet unravelled, nor can we effectively disguise this. Some cases of vitiligo, an idiopathic absence of pigmentation in localized areas of skin, do recover spontaneously, but other are permanent. The treatment with dihydroxyacetone is not, in my view, very helpful as it is most difficult to obtain the right shade of colour. The patient needs something to paint on his skin, perhaps daily, which he can adjust to his own colouring; the shades given by dihydroxyacetone do not really approximate closely to natural skin.

## DISCUSSION

Mr. I. Stead: In view of the comments in page 35 on antibiotics and hydroxyquinoline derivates, do you suggest that quaternary ammonium salts are the most suitable agents for application to the skin? If this is so, could you give me grounds to substantiate this?

The Lecturer: In the early days there were a number of difficulties from agents included in these quaternary ammonium salts which gave rise to sensitivity. I think this has now been largely overcome. I also think that these agents may produce an irritant effect in areas of skin which are closely together. They are certainly less sensitizing than the antibiotics.

Mr. V. C. H. Brockwell: Surgical scrubs based on hexachlorophene are widely used in British hospitals. A report (12) suggested that such items based on an anionic sulphonate emulsifier giving a neutral pH were less prone to cause irritation than products employing solid soaps. Do you have any information concerning the use of surgical scrubs in the treatment of acne infections? Would you like to comment on the adaptation and extension of such formulations for use as shaving creams?

Secondly, is it possible that photosensitization may be due to the combination of phenolic antibacterials with emulsifiers which necessitate a high pH?

The Lecturer: I strongly support what you say about surgical scrubs incorporating hexachlorophene. We use these for treatment of acne and patients find them helpful for cleaning. There are some people who find excessive use of soap somewhat harsh to the skin, and this anionic detergent is extremely well tolerated. Untoward effects are extremely rare, but I have seen a case where a lady presented a most extraordinary appearance after using one of these agents. Just along the hair margin she had a linear area of hyperkeratosis. It looked like excessive dandruff stuck onto the skin, and was certainly the result of treatment; on stopping, it receded. It has been shown that some of these anionic detergents do have a hyperplastic effect on the sebaceous gland. It did not react elsewhere. One has the impression, however, that some other people seem to complain of a little excessive

---

(12) *Brit. Med. J.* **1** 1254 (1963).

greasiness of their skin which may link with Skog's work that anionic detergents do have a hyperplastic effect upon sebaceous glands.

I believe that hexachlorophene and the *Parabens* are already used as antibacterial agents in shaving creams. I should have thought that people who have the type of skin which easily gets infected, or that which does not stand up to over-washing, might well be helped by putting an anionic detergent into shaving cream.

I am unable to answer your last question.

DR. H. W. HIBBOTT: I would like to make two comments. As I was listening to you I felt that we had a refreshing change in the dermatologist's outlook towards cosmetics. Apart from a slight indictment of bergamot you have not come down heavily on cosmetics as a great cause of trouble for the medical profession, very contrary to some lectures we have listened to in this Society from dermatologists. I think this represents a change to which this Society has been looking forward for some years. Looking at some of your rather wonderful slides, even when we saw lips in very bad condition you did not blame it on lipsticks. In this case, too, I feel that lipsticks, apart from being quite glamorous, are in fact very good lip salves and women are a very lucky half of the population in being able to wear them. I was very impressed by your outlook towards the cosmetic industry, and I feel that we ourselves are showing that we are really thinking hard about possible adverse effects on the skin, and that the results we are getting are showing up to the medical profession.

MR. B. CHAMBERS: Can you suggest the main cause of itching which accompany acute cases of dandruff?

THE LECTURER: Dandruff comprises dead cells (dander) which are being exfoliated and are being shed as a result of proteolytic enzymes. As a result you are bound to get some itching sensation as a normal state of affairs. Itching in the perianal region is very commonly due to bacterial breakdown of protein. Bacteria can grow very easily in a greasy, sebaceous area, and once you have a combination of desquamated cells with sebum you have a medium in which organisms will grow, and itching results. I would have thought that head itching is very often related to staphylococcal or other infections. You can, however, get emotional itching of the head, which may be due to some alteration in tension in the erector pili muscle, the hair standing on end through nervous sympathetic stimulus when you get anxious. People also go white due to nervous vagotonic influences. Thus a state of tension affecting the hair muscle will produce itching. It is very common for people to scratch their head in order to get rid of their tension.

MRS. H. BUTLER: According to you, as I understand it, some irritation is caused by blocking of the sweat gland. Is it not also caused by changes of temperature? I know a man who only gets severe itching in frosty weather, leading to eczema when he gets in front of a hot fire. That is not necessarily blocking of the sweat glands, is it?

THE LECTURER: This is another problem; the vascular supply of the skin differs in many places and once the skin is damaged the vessels become unstable and will leak. The response to histamine is also different. If you burn your hand, the result of that burn may lead to an unstable bit of skin which will flush up easily for as long as three years afterwards. With a winter eczema the vessels underneath it are equally unstable, and will flush up and leak more easily. In front of a fire the vascular changes may themselves increase the temperature and congestion, which will press on nerve fibres and cause itching. You are quite right – itching is much more easily elicited at high than at low temperatures.

MRS. H. BUTLER: Why does this only happen during frosty weather?

THE LECTURER: The skin gets dehydrated and therefore little spicules of keratin are standing up, thus the skin is non-intact and more easily injured by the friction of the clothes.

MR. A. G. MCGEE: Would you care to expand on your statement in page 35 that "phenol and other coal tar distillates are much less likely to irritate though a few are intolerant"?

THE LECTURER: Phenol and coal tar distillates can be both irritants and sensitizers, but are mainly irritants. The majority of individuals are unable to tolerate tar on skin. The problem is that the more you remove the phenol, which has an anaesthetic effect upon the nerve fibre, the less anti-itching effect is obtained. People who are intolerant of the tar acids are not going to be helped by removing the phenol component, because it is going to be less effective for them. Summarizing, crude coal tar is by far the most effective antipuritic agent – but the more it is purified the less anaesthetic effect does it have upon the nerve fibres.

MR. C. PARRY: What is your opinion about the suitability, and the possible mode of action of the purported hormone creams?

THE LECTURER: There is no doubt that hormones are very easily absorbed through the skin, and as they are absorbed they can produce both local and systemic effects; if a patient is taking hormones for any other reason, you may get a summational effect. I believe I am right in saying that at the control trial of release bleeding at the menopause with hormone cream, and an emolient alone, the results did not seem to be very significant. It was thought that the main effect of the hormone cream related to the hydration effect of the keratin of the collagen. I fail to see how you are going to alter the collagen degeneration a great deal in the older person, though I think you can do something in the younger person.

*J. Soc. Cosmetic Chemists* **17** 45-56 (1966)

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

G. W. SCOTT BLAIR*

*A lecture delivered before the Society on 7th October 1965.*

**Synopsis**—In all traditional, and even in some modern industries, the properties of materials and products are assessed by experts handling them. This is not in itself a bad thing but experts are becoming increasingly difficult to find and it is useful both for the craftsmen themselves and for those working in their absence to be able to compare such subjective assessments with physical measurements and chemical analyses. This paper is concerned with one group of "properties" commonly called "consistency." One must first ask whether the sensations perceived by the experts are themselves quantitatively measurable and, if not, how do we regard the judgements which they are undoubtedly able to make? A second question follows: By what combinations of stresses, strains and times do people assess consistency when they squeeze materials by hand? Are such combinations dimensionally similar to those which we use to define such physical properties as viscosity and elastic moduli? What mathematical and statistical techniques are required to describe the judgements offered?

Finally, the implications of psychorheology to the practical chemist or physicist working in a traditional industry are discussed.

Some years ago, I had the privilege of addressing you on the rheology of pastes, etc. (1) and now I should like to discuss how physical, and particularly rheological properties of materials, as measured by instruments, may be related to the subjective assessment of consistency by handling materials. Consistency has been defined as "that property of a material by which it resists permanent change of shape . . . defined by the complete flow-force relation"; but, in fact, the word is often used in an even wider sense. I have argued elsewhere (2) that rheologists require two types of technical terms – those which express precisely in c.g.s. units the properties of materials, such as

---

*National Institute for Research in Dairying, Shinfield, Reading.

viscosity, elastic moduli, relaxation times, etc., and terms which denote general similarities of behaviour, such as consistency, body, etc. If we give these latter terms, which I have called "denotative"* precise physical definitions, we shall have to invent new terms to replace them. It is better to invent new terms for the "connotative" physical properties where these are needed. So we will keep "consistency" as a very general term. It is the purpose of rheology to express the consistency of materials by means of numbers and this can, of course, be done both by subjective assessments and by instrumental tests. The question arises whether we can regard as a true "measurement," numbers which are scored by subjective tests, e.g. "very firm = 5, firm = 4, medium = 3, soft = 2, very soft = 1." I think we must accept the word "measurement" in its widest sense, so long as we are careful to appreciate that there is a hierarchy of types of measurement and that certain statistical treatments are applicable only to certain types of measurement.

It is also interesting that there is a hierarchy of the senses. An appreciation of the visual arts and of music is always regarded as desirable. Exact science is based almost entirely (some say entirely) on visible pointer readings for which we require only one colour-blind eye. A few scientific measurements, such as electrical resistance, are sometimes made through hearing. It is hard to find exact physical correlates for taste and still harder for smell, and the perfumers and restaurateurs will agree that there is still some prejudice against too great an interest in their products. Aesthetics deals hardly at all with the "feel" of materials. Is there any explanation for this strange parallelism? In our own day, the most intensive studies in this field of measurement theory have been made by S. S. Stevens (3)†, who defined "measurement" as "the assignment of numerals to things so as to represent facts and conventions about them." Although he has later proposed a somewhat more complex classification, his earlier grouping of types of measurement will serve for our present purpose. Stevens originally proposed four types of measurement, easily memorized because their initial letters form the French word for "black" (NOIR).

*Nominal* measurements, which some of us would hardly include as measurements at all, represent the arbitrary numbering of people or things

---

*The terms "denotative" and "connotative" have changed their meaning somewhat in the course of time (2).

†Stevens has published so many admirable papers on measurement that it is hard to know which to quote. Perhaps the best fairly recent expression of his views is to be found in (4).

and this really does no more than substitute a number for a name, as is sometimes done in the army or in prisons.

*Ordinal* measures are well illustrated by the scoring for firmness discussed above. There is no evidence that the numbers $5-1$ are evenly spaced and we cannot write, for instance, $5-4=2-1$; but the order is meaningful (5).

*Interval* scales, as the name implies, presume an equality of interval between the members, e.g. degrees on the Fahrenheit temperature scale, but the zero is arbitrary and sometimes indeterminate. Interval scales cannot be inter-converted by a single multiplication, whereas the highest category, *ratio* scales, such as lengths, masses, degrees Kelvin, etc., can.

Thus, if we ask the old question "Can sensations be measured?" Stevens would reply that it depends on what type of measurement you have in mind. This is, I think an appropriate stage to turn back to the earlier history of this controversial question, though only a very brief outline can be given here and some of the story is doubtless already well known to you [if not, it can be found in a book by Boring (6)]. In 1834 Weber found an empirical experimental law that the just noticeable difference (j.n.d.$\Delta$E) in the intensity of a stimulus, say a beam of light, is proportional to the intensity (E) of the stimulus. This is approximately true in many cases and there can be no theoretical objection to it in so far as it works. However, in 1850 (apparently unpublished until 1860) Fechner extended the "law" by making certain assumptions which were strongly challenged by many workers, including Tannery (1875) and later by Bergson (7).

Fechner assumed that our consciousness of an increase of stimulus is produced by an increase of sensation ($\Delta$S). It is further assumed that equal increases in j.n.d.'s correspond to equal increments of sensation so that $\Delta S = C\frac{\Delta E}{f(E)}$, C being a constant. The deltas are then arbitrarily replaced by d's and, assuming Weber's law, we have, by integration, $S = C \ln (E/Q)$, Q being a constant. This very dubious equation is, unfortunately, often linked with the name of Weber as "the Weber-Fechner law."

Tannery and Bergson claimed that sensations are not "quantities" at all and cannot, therefore, be expressed numerically.

Delboeuf, in Ghent and later in Liège, added a number of terms to Fechner's equation, mainly to obviate troubles with limiting conditions. He also performed experiments in which he claimed that it was possible to test his modification of Fechner's "law." It is, in fact, possible to persuade subjects to judge a stimulus as being twice as great or half as great as a control stimulus and so to calculate Fechner's "constant." Meanwhile Plateau, a fellow-countryman of Delboeuf's, proposed a double logarithmic (power) relation to replace the single logarithm of Fechner, though he later repudiated the idea. (The power relation may have been proposed independently by Brentano.)

I tell this brief story because it has a striking counterpart at the present time and the close parallelism with the earlier controversies appears to have been missed. Stevens (8) described many experiments and concluded that, for most (but not all) stimuli, the double logarithmic law is valid. Recently, however, Treisman (9–11) has criticized Stevens on the grounds that no experimental device can distinguish between the two equations. One cannot regard the responses of subjects as scientific observations. Dr. Treisman has kindly explained his ideas personally to me and it seems to me that, fundamentally, his objections differ little from those of Tannery (12)*. Stevens (13) has very naturally replied on much the same lines as did Delboeuf, that his equations are derived from experimental data and are not artefacts. The debate continues!

Meanwhile, whether sensations are truly measurable quantities or not, we can certainly record what people say that they feel. In a lighter vein:

There once was a craftsman of Deal
Who judged all his products by "feel"
But he spent his brief leisure
In trying to measure
Sensations he knew were not real.

Seriously, however, in all the traditional industries, which certainly include cosmetics and dairying (and even some of the new industries) the craftsman still judges the consistency of his materials and products by "feel" and it is the business of the physicist (rheologist) to try to design instruments which will give measures at least on an interval scale to supplement the craftsman's ordinal assessments. I particularly stress "supplement" because I think it no more likely that such instruments will replace the craftsman than that the clinical thermometer and the sphygmomanometer will replace the family doctor. Yet no "G.P." would be without these instruments today. I first came across this problem in the bread-making industry and realized that the rheologist cannot deal with such matters alone. I had the good fortune to have the late Professor

---

*Bergson's criticism was rather different. He believed that measurable quantities must be able to be simultaneously present "in space." Stimuli can be so present but sensations cannot. This is not Treisman's point.

D. Katz to study the baker while I studied the dough and he published a fascinating account of his investigations (14). After a somewhat similar study on heather honey (assisted by Brother Adam of Buckfast), I moved, in 1937, into the dairy industry and it seemed to me that the first thing we should find out was what degree of difference cheese-makers and others could detect in viscosity and elasticity when squeezing small samples of "perfectly" viscous and elastic materials between the fingers. (Strangely enough, the consistency, or "body" of cheese is very important, not so much directly to the consumer, but in controlling the growth of the micro-organisms that make for the required development of flavour and odour.) For this purpose, we made small cylinders (spheres in the earliest experiments) of a truly fluid Newtonian bitumen diluted with oil to different, very high viscosities and of rubber, filled so as to have different elastic moduli, comparable in firmness to cheddar cheese. Rubber is not a perfect elastic solid and it also perishes with time, so we later used small steel springs encased in bandages and with firm plastic end-pieces. Subjects were given pairs of samples and asked to judge which was the firmer after squeezing between the finger and thumb with as steady a pressure as possible. They were also asked to use about the same pressures throughout the tests. We found (15) that the average subject could distinguish differences in elastic modulus about three times as small as were the distinguishable differences in viscosity and that skilled cheese-makers were no better than other people at these tasks (*Fig. 1*). The only group that showed superiority was a number of routine analysts, from which we concluded that a patient and unhurried mental set was the most important

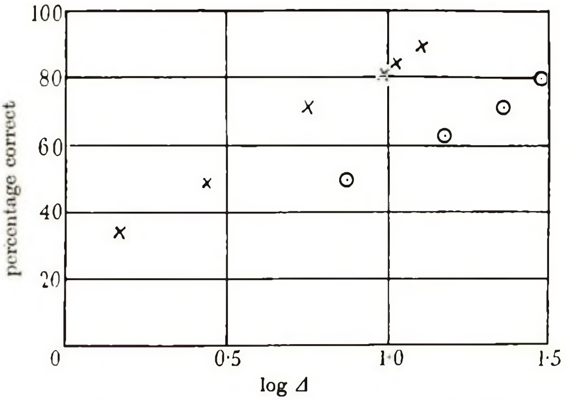


*Figure 1.* × compression modulus; ⊙ viscosity.

criterion for success. Later we tried the rather strange experiment of asking subjects to compare a bitumen in one hand with a rubber in the other, changing hands and repeating the squeezing before giving a judgement. I will not here list all the obvious precautions about temperature changes, etc., for which see (16). Here, of course, our subjects are trying to compare the magnitude of an elasticity with that of a viscosity, which is physically contrary to the principle of dimensional homogeneity. Apart from a few worried physicists, however, the subjects readily gave answers but these were dependent on the length of time allowed for the squeezing, which was controlled by a metronome at $t_c = \frac{1}{2}$, 1, 2 and 4 sec. As will be seen from *Fig. 2*, a graph of "percentage bitumen softer" answers, plotted against $nt_c$ (where n was the elastic modulus of the rubber) gave unique sigmoid curves which, on plotting logarithms of $nt_c$, could be made fairly straight throughout most of the field. (Later, my colleague Dr. R. Harper (17) calculated much more satisfactory analyses for such curves.)

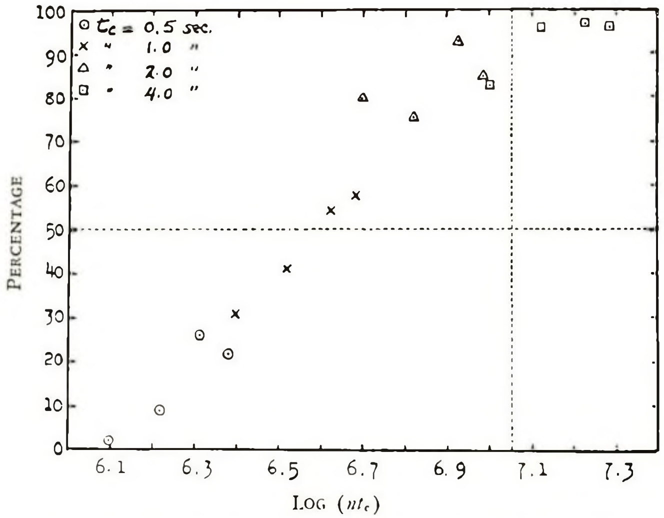


*Figure 2.* Results of simultaneous comparisons with two compressions.

One might suppose that, under such circumstances, subjects would give equality at the point when the compression (strains) on the two materials were the same at the end of the squeezing, but this is definitely not the case and we had to ask ourselves "by what are the subjects judging firmness?" To answer this question, we selected a number of high polymers which obeyed the very simple equation $\sigma = \psi^{-1}t^{k}S$ where $\sigma$ is strain, t is time, S is stress and k is an exponent. (In modern times, we should use different symbols but it is simpler here to keep to those in the original papers.)

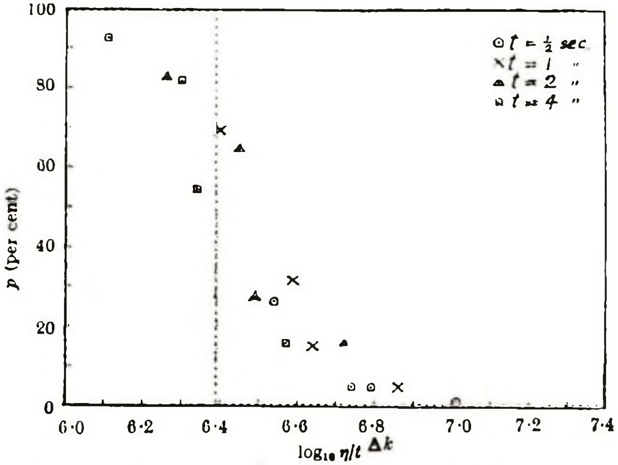
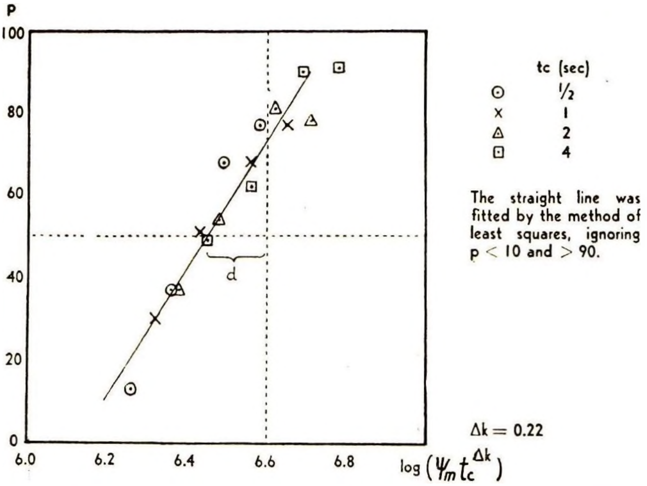


*Figure 3.* The dotted lines represent the curves obtained from the data from the compression machine.

*Fig. 3* shows a comparison between an unvulcanized rubber, the value of k, determined on a rheometer, being 0.50 and four samples of truly fluid bitumen (k = 1) having different viscosities (18). The "bitumen softer" answers are plotted as a percentage (p). A rather similar curve is shown in *Fig. 4* in which a plasticine-*Vaseline*-rubber mixture with k = 0.22 was compared with four different rubber samples (k = 0).

I will not give you the details of how we dismissed all the more obvious explanations of these phenomena. Suffice it to say that we were forced to the rather strange conclusion that subjects were judging neither by the amount nor by the rate of deformation under (as far as possible) constant stress but by intermediate entities. The equation given above, to which our "complex" materials conformed, is a simplified version of one proposed by Nutting (19) in which stress also has a fractional exponent ($\beta$) though $\beta$ may be $> 1$. Nutting's equation is itself a special case of a much more complex equation involving fractional differential coefficients. For a full account of these equations, the reader is referred to Harper (17). All we need say here is that we saw no reason to suppose that subjects handling materials should base their judgements of firmness on whole-number differentials of strain with respect to time. The "time" is, in any case, the Newtonian time of the clock and our subjective time-



The straight line was fitted by the method of least squares, ignoring $p < 10$ and $> 90$.

*Figure 4.* Results of a comparison with respect to the 'firmness' of rubber and bitumen (main experiment').

judging mechanisms do not depend on mechanical clocks. We rightly retain Newtonian time for our physical experiments (I have been wrongly accused of denying this!); but, if we try to apply this time-scale to subjective judgements, we cannot expect to get whole-number differentials (20,21). Fractional differentials are difficult to define and their use has not been followed up*, though the application of these "intermediate entities" is not limited to psycho-physics.

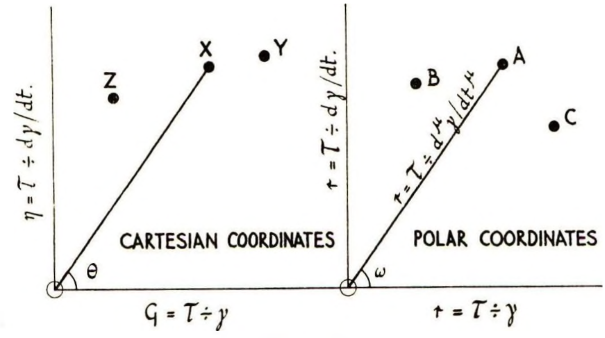


*Figure 5.*
An illustration of principle of intermediacy.
Burgers bodies X, Y, Z Complex bodies A, B, C

A simple way of picturing what I have called "intermediacy" is seen in *Fig. 5* (22). If we have a number of samples of some material X, Y

---

*My friend Mr. A. Graham has inverted the process and made good use of fractional integrals for studying the creep of metal alloys.

and Z, the behaviour of which can be described in terms of simple models of viscous and elastic elements in series and/or in parallel, we can make a diagram, using Cartesian coordinates, plotting the elastic modulus* against the viscosity ($\eta$). If we join these points (as X is joined in *Fig. 5*) to the origin, the tangent of the angle ($\theta$) gives us a measure of some relaxation or retardation time of the system and the position of X specifies the behaviour of the material. If, however, the samples (A, B, C) are too complex rheologically to be easily described in terms of a few viscous and elastic units, we can use *polar coordinates* (so that the diagrams are really quite different) and again plot $\sigma/\varepsilon$ along the horizontal axis and $\sigma/\dot{\varepsilon}$ on the vertical axis. The straight line is rotated through an angle $\omega$ so that the position of A lies in a continuum between the viscous and elastic conditions. The "radius vector" OA is analogous to both $\eta$ and G. For purely viscous systems, we have points on the vertical line such that $\sigma \div d^1\varepsilon/dt^1$ is constant and for elastic systems, points along the horizontal axis such that $\sigma \div d^\circ\varepsilon/dt^\circ$ is constant. For the complex materials, $\sigma \div d^\mu\varepsilon/dt^\mu$ is constant (where $1 > \mu > 0$) and $\mu$ will depend on sin $\omega$. The length of the line OA represents the intensity of a property ($\chi$) which approximates to a viscosity when $\sin \omega = 90^\circ$ and to an elastic modulus when $\sin \omega = 0^\circ$. It is clear that we must be careful about the dimensions of $\chi$, which are not constant but depend on the value of $\omega$. Dingle (23) has shown conclusively, however, that here there is no breach of dimensional homogeneity, nor is the treatment (as has been alleged) in any way unsound. It is simply that whereas we describe ordinary physical properties by means of one number in some arbitrary system of units (say 100 poises for a viscosity), these "quasi-properties," as I have called them, have to be described in terms of two or more dimensions of space.

My own experimental work in the field of psychorheology came to an end some fifteen years ago, but my colleague Dr. Harper, working both alone and with Professor Stevens, has carried the researches considerably further (24). Measurements of hardness were made on materials covering a wide range, with a ball compressor. The relationship between measured and judged hardness was found to follow Stevens' power-law. Comparisons were also made with loudness of (white) noise. In another paper, Stevens and Guirao (25) asked subjects to assess viscosities of silicone liquids ranging from about 0.1 to 950 poises. *Fig. 6* shows the log-log relation between the subjective assessment and the physical measurement. "Each point represents the geometric mean of 20 numerical judgements

---

*In this much more recent paper, G is shear modulus, $\sigma$ is stress, $\varepsilon$ is strain, $\dot{\varepsilon}$ is $d\varepsilon/dt$.

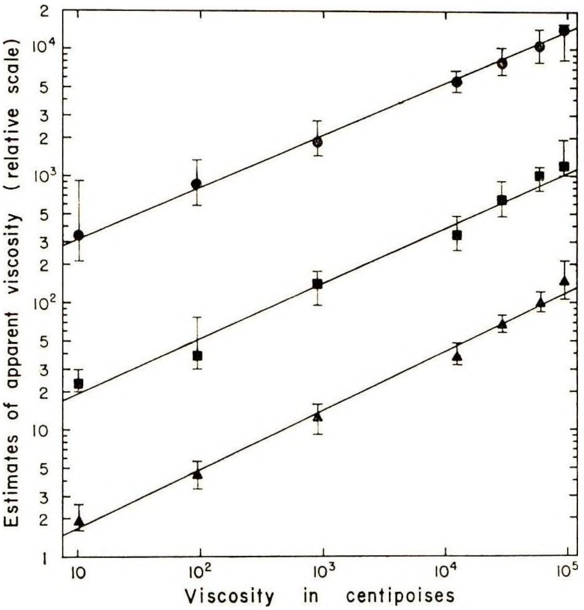


*Figure 6*

of apparent viscosity, two judgements by each of ten observers. Each power function represents a separate experiment. Circles: The observer watched the liquid while shaking or turning its container. Squares: The observers stirred the liquid while blindfolded. Triangles: The observers watched the liquid while stirring it. For clarity, the functions are separated vertically by one log unit. The exponents (slopes) are 0.42, 0.43 and 0.46. The vertical bars represent the interquartile ranges of the 20 judgements of each stimulus."

In conclusion, it would be well to try to see how these rather complicated experiments and theories can help anyone who is trying to relate subjective judgements to exact laboratory measurements, by either physical or chemical analysis.

Our own earlier experiments showed that although there is a very real superiority on the part of craftsmen in judging quality of dairy products, their actual sensitivity to small changes in consistency is no higher than that of the inexpert. Their skill lies in interpretation and in the formation of what Bartlett called "schemata" (following Head); that is, subconsciously retained information about the significance of sense-data. The "schema" is analogous to an instinct but is acquired and not inherited (26). A characteristic of experts is their unwillingness to analyse their general judgements of consistency into separate physical components. We once asked a number of cheese experts, and others, to score a batch of cheese separately for firmness, springiness and crumbliness. There was little physical correlation between these properties among the samples given and the inexpert had, in general, no difficulty in giving us separate orders for the three. But the experts always gave the same order; they could not get away from the combined concept of "body," which includes all that can be felt with the fingers. When we did get a number of separate subjective assessments of different rheological characteristics, as well as several physical tests, we generally sorted out the correlations, i.e. simplified the correlation matrix, by means of Multiple Factor Analysis; but I have already described this technique to you in some detail (1).

Just how the expert reaches his conclusions and interprets his sense data we do not know, but we used to think that such judgements are mainly concerned with kinaesthetic (joint and muscle) sensations rather than with cutaneous (skin) sensitivity. More recent experiments by Harper have, however, thrown some doubt on this conclusion. Much more work requires to be done. The rheologist, as a physicist, naturally likes his concepts and especially his definition of "physical properties" to come within the range of Continuum Theory. Properties should have well-defined dimensions, generally expressed in powers of mass, length and time, should be invariant to changes in coordinate systems, and so forth. Unfortunately, human beings do not judge consistency in these terms; or if they do try to do so, they are attempting to bridge the gap between subjective and objective measurements in a somewhat artificial way. Fundamentally, my own view is that the gap is unbridgeable but I am also quite confident that physical measurements, whether of primary physical properties or of more complex behaviour, can most certainly help – but not replace the craftsman. The greatest difficulty facing those working in this field is to persuade the craftsman that this is so and that we are not secretly attempting to replace him by machines.

(*Received: 7th October 1964*)

## ACKNOWLEDGEMENTS

The author gratefully acknowledges permission by the following to reproduce the illustrations:
The Royal Society for *Fig. 1*.
The Editor, *American Journal of Psychology*, for *Figs. 2* and *4*.

The Editor, *Nature*, for *Fig. 3*.
The Editor, *British Journal for the Philosophy of Science*, for *Fig. 5*.
The Editor, *Science*, and Prof. S. S. Stevens for *Fig. 6*.

## REFERENCES

(1) Scott Blair, G. W. *J. Soc. Cosmetic Chemists* **11** 181 (1960).
(2) Scott Blair, G. W. in Harrison, V. G. W. *Some Recent Developments in Rheology* (1950) (United Trade Press, London).
(3) Stevens, S. S. *Science* **103** 677 (1946).
(4) Stevens, S. S. Chap. in Churchman, C. W. and P. Ratoosh *Measurement: Definitions and Theories* (1961) (Chapman & Hall, London).
(5) Sheppard, D. *Brit. J. Psychol.* **45** 40 (1954).
(6) Boring, E. C. *A History of Experimental Psychology*, 2nd Edn. (1929) (Appleton-Century-Crofts, Inc. New York).
(7) Bergson, H. *Essai sur les données immédiates de la conscience* (transl. F. L. Pogson as *Time and Free Will* (1960) (Swan Sonnenschein, London).
(8) Stevens, S. S. *Psychol. Rev.* **64** 157 (1957).
(9) Treisman, M. *Brit. J. Philos. Sci.* **13** 130 (1962).
(10) Treisman, M. *Nature* **198** 914 (1963).
(11) Treisman, M. *Quart. J. Exper. Psychol.* **16** 11, 387 (1964).
(12) Tannery, J. Correspondence in *Revue Scientifique* reproduced in *Etudes Psychophysiques* by J. Delboeuf, Baillière et Cie, Paris (1883).
(13) Stevens, S. S. *Quart. J. Exper. Psychol.* **16** 383 (1964).
(14) Katz, D. *Cereal Chem.* **14** 382 (1937).
(15) Scott Blair, G. W. and Coppen, F. M. V. *Proc. Roy. Soc.* (B) **128** 109 (1939).
(16) Scott Blair, G. W. and Coppen, F. M. V. *Amer. J. Psychol.* **55** 215 (1942).
(17) Harper, R. *Amer. J. Psychol.* **60** 554 (1947).
(18) Scott Blair, G. W. and Coppen, F. M. V. *Nature* **149** 22 (1942).
(19) Nutting, P. G. *Proc. Amer. Soc. Test. Mater.* **21** 1162 (1921).
(20) Scott Blair, G. W., Veinoglou, B. C. and Caffyn, J. E. *Proc. Roy. Soc.* (A) **189** 69 (1947).
(21) Scott Blair, G. W. and Caffyn, J. E. *Phil. Mag.* (ser. vii) **40** 80 (1949).
(22) Scott Blair, G. W. *Brit. J. Philos. Sci.* **11** 272 (1961).
(23) Dingle, H. *Phil. Mag.* **40** 94 (1949).
(24) Harper, R. and Stevens, S. *Quart. J. Exper. Psychol.* **16** 204 (1964).
(25) Stevens, S. S. and Guirao, M. *Science* **144** 1157 (1964).
(26) Oldfield, R. C. and Zangwill, O. L. *Brit. J. Psychol.* **32** 267; **33** 58 113 (1942).

# Book reviews

## HISTONES AND OTHER NUCLEAR PROTEINS. H. Bush. Pp. xiii + 266 + Ill. (1965). *Academic Press, New York and London.* 76s.

Recent advances in molecular biology have shown how deoxyribonucleic acid (DNA) is the initiator of the chain of reactions which, through the biosynthesis of messenger ribonucleic acid (RNA), leads to synthesis of the cellular proteins.

Not all proteins in the cell are synthesized at the same time, however, or even at the same rate, and a mechanism must exist by which one set of reactions may be made several hundred times more active than another. There is evidence that the proteins of the nucleus play a part in this controlling mechanism; in particular, the basic proteins can be shown to have a suppressive action on some nucleic acid-induced reactions. There has consequently been a revival of interest in these proteins, and it is the object of this book to give an introduction to the current status of research in this field.

The greater part of the book concerns the basic nuclear proteins. A chapter deals with the protamines – no dynamic function has yet been demonstrated for these proteins, and they may serve only as carriers for DNA. Histones, which are more complex, and which occur more widely in plant and animal tissues, are dealt with at greater length. Chapters are first devoted to classification and to methods of isolation. The spatial relationships between DNA and histones are discussed, and it is shown that histones may help to maintain the coiled structure of the nucleoprotein. Evidence for the concept of histones as gene modifiers is then reviewed, following from the observation that histones can block RNA synthesis in systems containing DNA. The growth and functions of cells *in vitro* are also inhibited by histones; it is of interest that the antiviral substance, interferon, is a histone-like protein. Chapters on the primary structure of histones, and on their biosynthesis and catabolism, complete this section.

Work on acid proteins of the nucleus has not yet developed to the same extent. A chapter describes the state of research on their isolation, amino acid content, and biosynthesis. Finally, the enzymes of the nucleus are reviewed, with particular reference to those involved in nucleic acid synthesis.

Author and subject indexes are provided, and each chapter has an extensive list of references. The book provides a succinct review of the current position in a field which will certainly expand rapidly within the next few years. B. G. OVERELL.

## ADVANCES IN HETEROCYCLIC CHEMISTRY. Vol. 3. Editor: A. R. Katritzky. Pp. xiii + 421 + Ill. (1964). *Academic Press, New York and London.* 96/6.

The third volume in this series contains three reviews devoted to specific groups of heterocyclic compounds and four reviews dealing with topics of general interest in heterocyclic chemistry.

The three goups of compounds discussed are the Carbolines (129 pages) by R. A. Abramovitch and Ian D. Spenser; 1, 2, 3, 4 – Thiatriazoles (22 pages) by K. A. Jensen and C. Pedersen; and Pentazoles (11 pages) by Ivar Ugi.

G. F. Duffin reviews the Quaternization of Heterocyclic Compounds (56 pages); the Reactions of Heterocyclic Compounds with Carbenes (22 pages) are covered by C. W. Rees and C. E. Smithen; Applications of the Hammett equation to Heterocyclic Compounds (53 pages) is an excellent and useful review by H. H. Jaffe and H. Lloyd Jones; finally G. Illuminati presents a comprehensive survey of Nucleophilic Heteroaromatic Substitution (87 pages).

Each review is fully supported by references to original papers and the truly international character of this series is reflected in the authors of the reviews in this volume from Great Britain, U.S.A., Canada, Denmark, Italy and Germany. The volume concludes with comprehensive author and subject indexes.

Included in this volume are the lists of contents of Volumes 1 and 2 and also Errata to these volumes. This is a first class production and an excellent addition to the growing list of review literature. R. P. REEVES.

## NON-AQUEOUS SOLVENT SYSTEMS. Editor: T. C. Waddington. Pp. xiv + 408 + Ill. (1965). *Academic Press, London and New York.* 90s.

The book is organized into nine chapters – four dealing with protonic solvents, four with aprotic media and a final one on the solvent properties of molten salts. The editor has wisely recognized that it would not be possible to cover adequately the vast range of non-aqueous solvent systems in one volume; he has avoided a superficial discussion of this gamut and chosen instead to treat fairly exhaustively a limited number of solvents that are important *per se* and which may be held to exhibit type behaviour.

Liquid ammonia is worth a book in itself; a recent article (1), for instance, only covered the chemistry of inorganic reactions therein. Here those aspects susceptible to quantitative treatment are dealt with. First there is a considerable accumulation of physical, magnetic and spectroscopic properties and thermodynamic and electrochemical data for liquid ammonia; particularly useful is the list of half-wave potentials and the details of metal-ammonia systems. The balance of the chapter is concerned with a relatively comprehensive general survey of reactions in liquid ammonia; contrast is drawn with water as well as with less polar solvents. Finally the oxidation potential, ionic solvation, acid-base reactions, and the interaction of metals in and with ammonia are reviewed.

Despite the favourable ionic radii, the aggressive properties of hydrogen fluoride had until recently rendered it unpopular as a protonic solvent. The development of nuclear chemistry, and especially fluoroplastics resistant to HF, changed this dramatically. This chapter – by two workers at the Argonne atomic energy laboratory – begins appropriately with a discussion of apparatus and equipment adapted for conductimetric and spectroscopic studies, and then extensive physical and spectroscopic properties are set out. The ionised, and particularly the associated, structures of hydrogen fluoride and the nature of its acidity, are examined in detail. Examples of solutes in HF are taken from metals, interhalogens, proton acceptors (oxonium

---

(1) Fowles, G. W. A. and Nicholls, D. *Quart. Rev.* **16** 19–43 (1962).

formation), fluoride acceptors (mainly metal fluorides), salts resisting solvolysis and solution without ionisation. There is an interesting final section on biochemical studies. In a separate chapter other ionising hydrogen halides are considered as examples of very acidic solvents of low dielectric constant.

Sulphuric acid is the third protonic solvent of high dielectric constant to be examined – and at considerable length (88 pages and over 200 references). Solution mechanisms and conductimetric data are discussed for organic and inorganic acids, bases and non-electrolytes; a special section is devoted to sulphates and bisulphates. Physical and spectroscopic properties of sulphuric acid, and its solutions, are tabulated and then detailed consideration is given to a very wide variety of inorganic and organic solutes.

The other half of the book is concerned with aprotic solvents. In a chapter on coordinating solvents, the major media for inorganic studies, the "Solvent systems concept" (due to Gutman) is developed as a model of non-aqueous solvent behaviour. Spectroscopic, cryoscopic and conductimetric methods for establishing the existence of coordination are comprehensively reviewed whereafter the energetics of solvent-solute interaction and methods for recognition of the species present are described. Correlation of the solute products with solvent is examined for nine typical organic coordinating media. Liquid sulphur dioxide is taken as a typical aprotic solvent widely used for the study of organic reaction mechanisms. In two further chapters, apportioned to the halogens and interhalogens, and to the (Periodic) Group V halides and oxyhalides, the theory of halide ion dissociation and exchange is critically assessed. The final chapter reviews the chemical and physical properties and constitution of highly ionised and conducting molten salts. Examples are given of industrial applications, including the separation and extraction of metals.

This is a most readable and authoritative contemporary review of suitably representative non-aqueous solvents. The editor has cast his net widely to draw on the research experience of his 13 co-authors; one should not cavill at the occasional introduction thereby of trans-Atlantic terms, such as "vibronic spectra." The text is well illustrated with figures and the references are adequate for most purposes. This book may warmly be commended – although the price may well deter the less affluent specialists. G. F. PHILLIPS.

## INORGANIC CHEMISTRY. J. Bassett. Pp. viii + 347 + Ill. (1965). *Pergamon Press, London and Oxford.* 30s.

The stated intention of the book is to provide students with a concise and readable account of modern inorganic chemistry of a standard intermediate between school "Advanced level" and an Honours degree. It is written around the modern concept of the detailed electronic structure of the elements and their vertical, diagonal and horizontal relationships within the Periodic Table.

Part I is the essential prologue and the enunciation of basic principles in Chapters I and II is the key. They deal superficially with the simpler features of atomic structure, electronic configuration and the periodic classification. These vital precepts are perhaps a little too condensed and one might well criticize points of detail, e.g. (1) there is a constant lack of cross-references – as when the reader is told on page 31 of the importance of the Principle of Maximum Multiplicity in connection with paramagnetism and colour but has to read on to Chapter XI before finding a three-page dissertation thereon, (2) the significance of the K,L,M, etc., X-ray spectra series are neither explained in Fig. 1.5 nor related to the discussion of K,L,M, etc., electron shells in Chapter II, (3) in discussing quantum numbers, reference is made to the theoretical advances due to Bohr and Schrödinger but there is no mention of the significant experimental observations of Stark and of Zeeman. However, examples of the Pauli and Hund Principles are worked out in full for the K, L and M shells and the subsequent exposition of the periodic relations arising from the filling of electron sub-shells is most lucid.

The chapter on the chemical bond is particularly recommended – there is an eloquent discussion of the significance of ionic potential, electron affinity and lattice energy. Covalent bond formation, hybridization, electronegativity concepts and intermediate structures are also well summarized; it is not unreasonable to refer elsewhere for a mathematical treatment. Metallic and hydrogen bonds, however, are dealt with much more superficially. Particularly concise but clear is the exposition of ionic radius, radius ratio criteria and simple crystal structures. In Chapter V there is a short derivation of the stereochemistry of the non-transition elements in terms of the directional properties of covalent bonding and non-bonding hybridized orbitals. There is a brief discussion of oxidation and reduction, standard electrode potentials, the electrochemical series, and discharge potentials. Examples are given of the use of oxidation number in determining the stoichiometry of redox and disproportionation reactions. Chapter VI ends with a short reference to I.U.P.A.C. standard inorganic nomenclature. The last chapter of Part I comprises a general classification of the occurrence, enrichment, reduction and various techniques of purification of metals; a number of interesting contemporary examples are included.

The remainder of the book comprises a systematic study of the elements; the majority of those considered are dealt with by group presentation. The author paints with a broad brush, but this frequently results in very superficial attention. The emphasis is on the principles established in Part I, especially the electronic structure of the subgroup of elements being considered. As a compromise between the classical (see below) and a completely functional treatment of inorganic chemistry as in Ephraim (1), hybrides are classified and considered under hydrogen, but the most interesting are further discussed in the chapter for the appropriate element. Group Ia is only briefly treated but within Group IIa, vertical and some diagonal relationships are emphasized for different anionic and covalent functions. The first long period is taken as a systematic example of the transition, or "d block," elements. Serial properties such as ionic radii, oxidation states, magnetic behaviour and complex formation are reviewed (although ligant field theory is considered too complex for this text) and there is a short account of the major metals in that block, i.e. chromium, manganese, iron, cobalt and nickel. A separate chapter reviews the vertical relation of the coinage metals – copper, silver and gold – which possess the common system of a full 'd' shell and one subsequent 's' electron. Similar treatment is afforded the zinc cadmium mercury triad in Group IIb. The following chapters deal with the interrelation of the commonest elements in successive groups, viz. the boron aluminium pair, Groups IVb and Vb, oxygen and sulphur – of which the acids receive inadequate treatment, the halogens and (briefly) the noble gases.

This is a highly readable book, although the telegraphic style is slightly reminiscent of the lecture notebook, a reaction supported by the frequent use of abbreviations and

---

(1) Ephraim, F, *Inorganic Chemistry*, 4th Edn. (1943), *Gurney and Jackson, London.*

chemical formulae in the prose text. Unnecessary verbiage has been kept to the minimum. There is no doubt that there is a considerable gap between the classical serial treatment (occurrence, extraction, application and properties) of a few elements in isolation that once was presented, and enlightened teaching in schools and university. The lucid systematic presentation of this short book may well be the answer – but probably more for the sixth-form and scholarship pupil than the H.N.C. or B.Sc. General student who are equally the target of the author. Such students may, however, rely on this as a first year revision text and indeed many chemists long past their graduation might read Part I with interest. Certainly the soft cover, small size and bargain price should deter no student. G. F. PHILLIPS.

## BIOCHEMISTRY OF QUINONES. Editor: R. A. Morton. Pp. xvii + 585 + Ill. (1965). *Academic Press, London and New York.* 117/6.

Let no one be mislead by the title of this book and assume that it is devoted exclusively to biochemical topics. It also contains an impressive array of both synthetic organic and physical chemistry. For instance the chapter by R. A. Morton on the UV adsorption spectra provides a concise introduction to the theory of spectra, before passing smoothly to the particular requirements of the quinones. Thereafter there is little concession to the inexpert reader. There is a mass of data, sufficient to satisfy the most demanding scientists, critically examined and amply supported by numerous references. The same high standard is achieved throughout the book, which is arranged so that the subject develops logically. It starts with the identification of the quinones, then considers the chemistry and then the distribution. The biosynthesis is discussed next, and the latter half of the book is devoted to the very diverse biochemical functions.

The biochemistry of quinones is still not fully understood. For instance, while it is clear that the extraction of CoQ from mitochrondria inhibits the succinate oxidase activity, it is still not clear whether CoQ is on the main electron transport pathway. Similarly, knowledge of the vitamin E is also incomplete. Discussion continues as to whether there is some role other than pure *in vivo* antioxidant activity. What is the link with selenium? What is the basis of the synergistic activity in preventing muscular dystrophy? Much research remains to be done on this interesting class of compounds.

This volume will help in this respect since it contains a wealth of condensed information critically prepared by world experts in this field. There are many up-to-date references with comprehensive author and subject indexes. It is not an easy book to read, but it is invaluable as a work of reference and should be available to all those who are even occasionally involved with naturally occurring quinones. A.W.H.

## PROGRESS IN THE CHEMISTRY OF FATS AND OTHER LIPIDS, VOLUME VIII, PART 1: PHOSPHOLIPIDS AND BIOMEMBRANES. L. L. M. van Deenan. Pp. vi + 127 + Ill. (1965). *Pergamon Press, Oxford.* 50s.

This is part of the eighth volume in a series that began in 1952 but now seems to be published with more regularity, viz. three volumes in the last three years. The previous two volumes have been published in parts – no doubt a reflection of the growing activity in the field of lipid chemistry. The focus of interest in the series has shewn a gradual transition from fatty substances of vegetable origin or industrial significance to the function of lipids in biological systems. The present volume which continues that trend, may be of particular interest to cosmetic chemists concerned with the conditions of skin permeability.

This account of progress in lipid chemistry deals with the specific function of phospholipids in relation to cell membranes. The work is divided into three broad topics, of which the first occupies half the text. Detailed treatment is given to the lipid composition of cell membranes, of specialized cells such as erythrocytes, and of sub-cellular particles, e.g. nuclei and chloroplasts. The chemical structure of phospholipids and their relation with cholesterol and the nature and significance of the non-polar side groups are discussed.

It is generally agreed that the integral nature of cellular interfaces is due to a surface active function of phospholipids, i.e. by interaction with both lipid and protein structures. There is much more room for argument, however, when seeking to assign the nature and magnitude of the forces involved in associating and aligning the components of the membrane. Further, by no means all membranes appear to conform to the lipid "sandwich" model; non-lamellar structures and multi-unit associations are not uncommon. Thus in the second section, current theories are elaborated for the molecular arrangement of lipids within biomembranes and as constituents of enzymes. Reference is made, with suitable illustrations, to powerful physical techniques (such as electron microscopy and X-ray diffraction) and micro-biophysical studies in relatively simple systems.

A natural membrane is a metabolically dynamic system – phospholipids may assist in this fluidity by enzyme transport at the boundaries. The final section, therefore, gives a fairly brief account of some of these dynamic aspects of membrane phospholipids, notably their participation in several related synthetic and catabolic pathways and their importance in a variety of membrane transport processes.

This survey emphasizes that research into the properties and composition of cell membranes should enhance our knowledge of the relation of structure and function of lipids within membranes. Nevertheless one must share the author's conclusion that in the vast field of interdisciplinary research on molecular architecture and functioning of biomembranes, many biological, chemical and physical problems with lipids still challenge the investigator. This is a slim and relatively expensive volume – it is well written and illustrated although the presentation remains very much for the specialist. Though nominally part of the Progress in Lipid Chemistry series, it may well be read in isolation by all concerned with cytochemistry. G. F. PHILLIPS.

1965 SOIREE

The President presenting the Diploma to Miss H. Birrell, winner of the £5 prize.

*Bristol Evening Post photograph*

BRISTOL CIVIC RECEPTION

The Pearl Sword being examined during the Civic Reception by (from lt. to rt.) the Sheriff of Bristol, the Lord Mayor, the President of the Society, Dr. A. W. Middleton (Vice President), and Mr. A. Herzka (Hon. Editor).

# Society of Cosmetic Chemists of Great Britain

## 1965 SOIRÉE

The Society's second Soirée was held on 9th October 1965 at the School of Pharmacy, London, when a number of members and friends spent a pleasantly informal evening together.

During the course of the evening Diplomas were presented to several of the candidates who had been successful in the Society's 1965 Diploma Examinations. Miss Helen Birrell, as prize-winning student of the year, was also awarded £5.

The rest of the evening was taken up with dancing together with two diversions in the form of a smelling competition and a show of slides taken during the visit to the 1964 I.F.S.C.C. Congress in New York.

## SYMPOSIUM ON PHYSICAL METHODS

The Symposium on Physical Methods which took place at Bristol on the 16th and 17th November was attended by 84 participants, including visitors from Belgium, Germany, South Africa, Sweden and Switzerland.

On the afternoon of the 16th November, symposium participants visited the laboratories of the School of Pharmacy, Bristol College of Science and Technology, Ashley Down, by kind invitation of Professor D. A. Norton.

During the evening of 16th November, participants attended a Civic Reception at the Council House, given by the Lord Mayor of Bristol, Alderman T. H. Martin, M.B.E.

## 1966 PROGRAMME

Lectures will be delivered on the following Thursdays:

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

6th January
*The economics of research*
C. Freeman, B.Sc. (National Institute of Economic and Social Research)

3rd February
*Perfumery lecture*
M. Jordi-Pey (Firmenich & Cie., Geneva)
(Jointly with British Society of Perfumers)

3rd March *MEDAL LECTURE:*
*The changing face of organic chemistry*
Lord Todd, F.R.S. (Professor of Organic Chemistry, University of Cambridge)

31st March
*Some aspects of laboratory planning*
D. J. Alexander, B.Sc. (Unilever Research Laboratory, Isleworth)

*FILM EVENING:* Thursday, 19th May.

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

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

## SYMPOSIUM ON COLOUR

A Symposium on Colour will be held at the Grand Hotel, Eastbourne, Sussex, on 26th and 27th April 1966. Registration forms and full details will be available from the General Secretary at the end of January.

## 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

## P. J. Fowler

It is with regret that we have to record the death of Mr. Philip Fowler at the age of 80 years, on 21st November 1965, as a result of a road accident in Rome, Italy.

Mr. Fowler was a Founder Member of the Society and a Member of the Pharmaceutical Society of Great Britain; he acted as Honorary Treasurer of our Society from 1954–55.

Educated at the William Ellis School, Gospel Oak, he was employed for some years by Manetti Roberts in Italy, and in 1932 he joined the Pond's Extract Co. where he was responsible for the then new factory organisation in the capacity of works director. After his retirement in December 1953 he returned to Italy to live in San Remo.

He continued to take an interest in the affairs of the Society and kept up his membership to the end.

## GENERAL NOTICES

**Publication dates: The "Journal of the Society of Cosmetic Chemists" is published every four weeks.**

**Five issues for the Society of Cosmetic Chemists of Great Britain**
**by Pergamon Press Ltd., Headington Hill Hall, Oxford, England.**

**Six issues by the Society of Cosmetic Chemists**
**from 201 Tabor Road, Morris Plains, N.J., U.S.A.**

**Two issues for the Gesellschaft Deutscher Kosmetik-Chemiker, e.V.**
**by Dr. Alfred Hüthig Verlag, Wilkenstrasse 3-5, Heidelberg, Germany.**

| *Issue No.* | *Publication Date* | *Country of Origin* |
|---|---|---|
| 1 | 8th January | Great Britain |
| 2 | 5th February | U.S.A. |
| 3 | 4th March | U.S.A. |
| 4 | 1st April | Great Britain |
| 5 | 29th April | Germany |
| 6 | 27th May | U.S.A. |
| 7 | 24th June | Great Britain |
| 8 | 22nd July | Great Britain |
| 9 | 19th August | U.S.A. |
| 10 | 16th September | U.S.A. |
| 11 | 14th October | Great Britain |
| 12 | 11th November | Germany |
| 13 | 9th December | U.S.A. |

*Advertisements* : All enquiries regarding advertisements in the British Editions of the Journal should be addressed to Mr. J. V. Robinson, Pergamon Press, Ltd., 4 & 5 Fitzroy Square, London, W.1.

*Subscription* : All members of the Society of Cosmetic Chemists of Great Britain receive one copy of each edition free. Further copies at non-member rates. Non-members: £10 per annum, post free, or £1 per issue, post free.

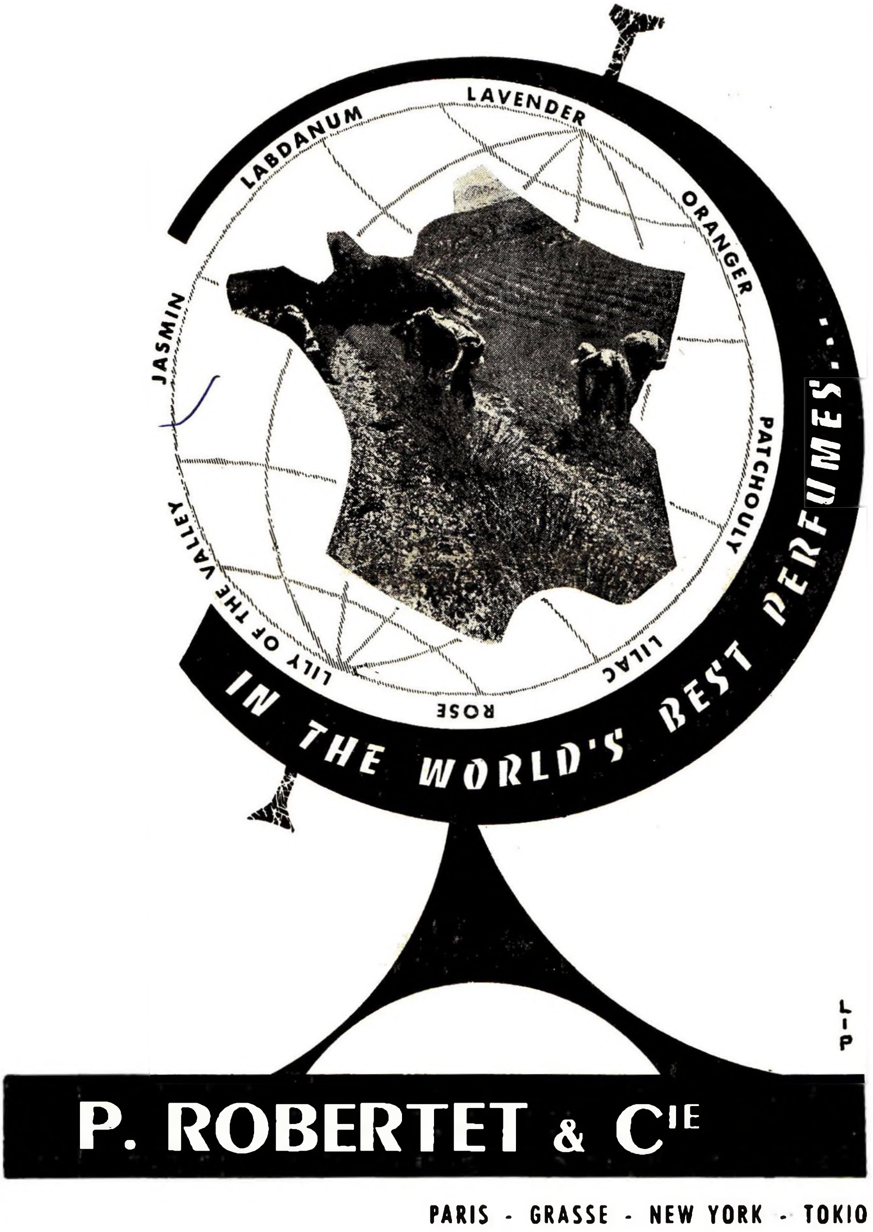
*Missing Numbers* : **Journals are despatched at Printed Paper rate. Claims for missing numbers can be entertained only from subscribers in the country of origin of the particular issue, and must be made within 30 days from date of issue.** Members and subscribers are urged to give notice of change of address to the Publication Offices.

*Responsibility for statements published* : The Society of Cosmetic Chemists of Great Britain and its Hon. Editor assume no responsibility for statement or opinions advanced by contributors to this Journal.

*Lectures* : The Society shall have the right of first publication of any lecture or address delivered before it, but does not undertake to publish any given matter.

*Copyright* : Reproduction of synopses, duly credited to the authors and THE JOURNAL OF THE SOCIETY OF COSMETIC CHEMISTS, is permitted. Digests of articles not exceeding 400 words may be published, duly credited to the author and THE JOURNAL OF THE SOCIETY OF COSMETIC CHEMISTS. Reprinting or extensive copying (whole pages or articles) is forbidden, except by special permission in writing, from the Hon. Editor. Any republication must indicate the source of the original paper. The copyright of all papers published in the British Edition belongs to the Society of Cosmetic Chemists of Great Britain. Authors must obtain written permission from the copyright holder to reproduce illustrations or quotations from other sources.

*Manuscripts* : These should be in accordance with the "Directions for Preparation of Manuscripts," copies of which are available from the Hon. Editor, Ashbourne House, Alberon Gardens, London, N.W.11.



---

Published on behalf of the Society of Cosmetic Chemists of Great Britain by Pergamon Press, Ltd., Headington Hill Hall, Oxford. Printed and Bound by Cheltenham Press Ltd., Swindon Road, Cheltenham and London, Great Britain.