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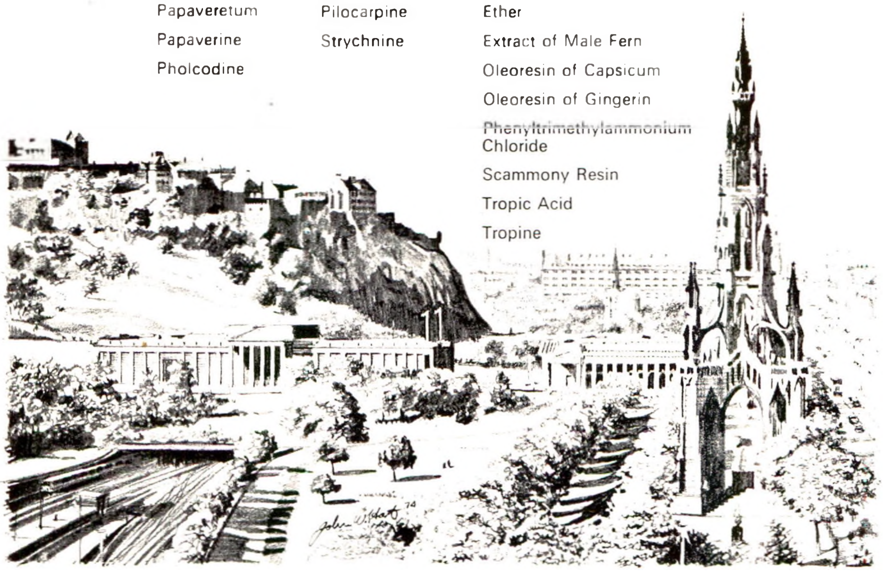
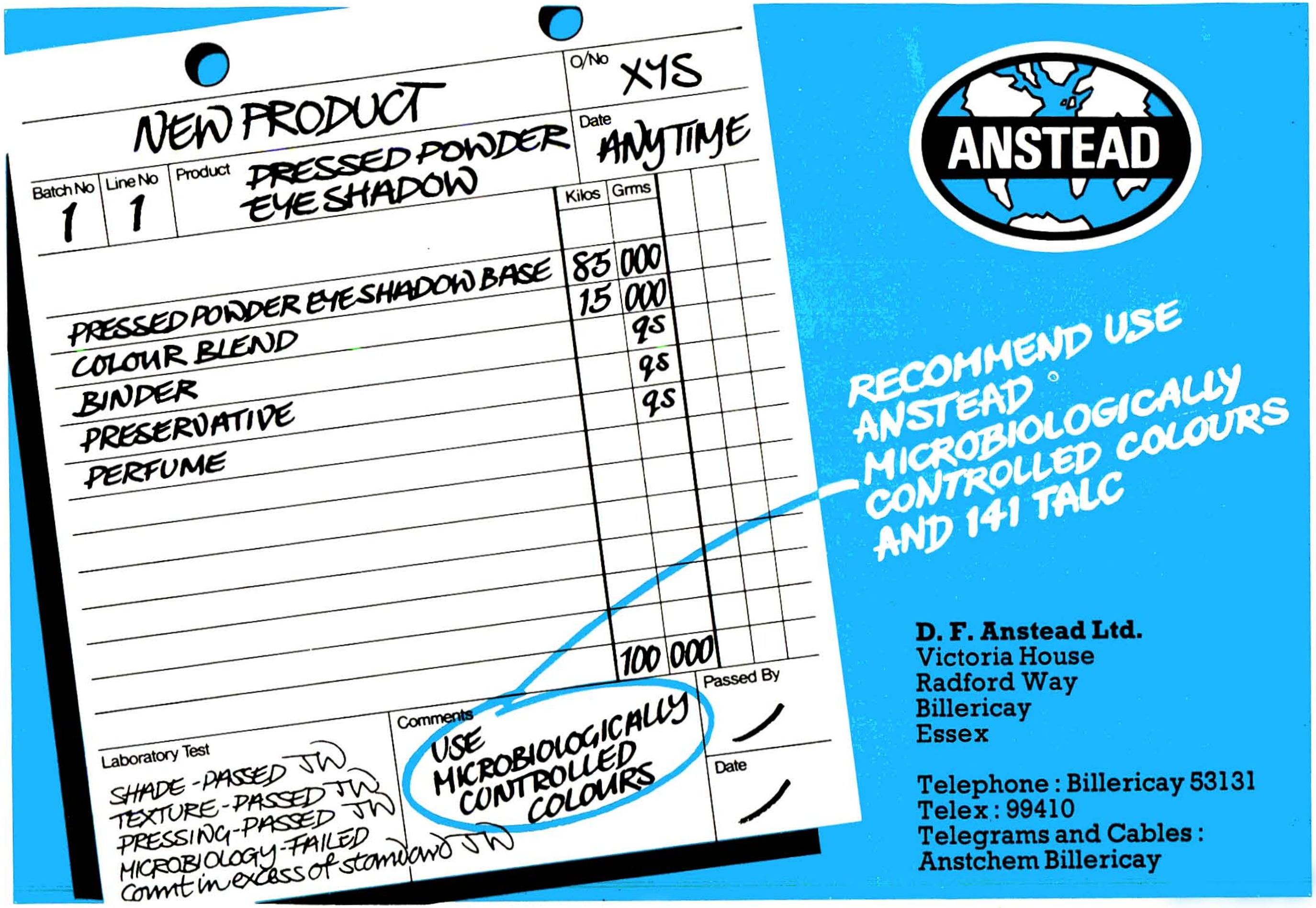
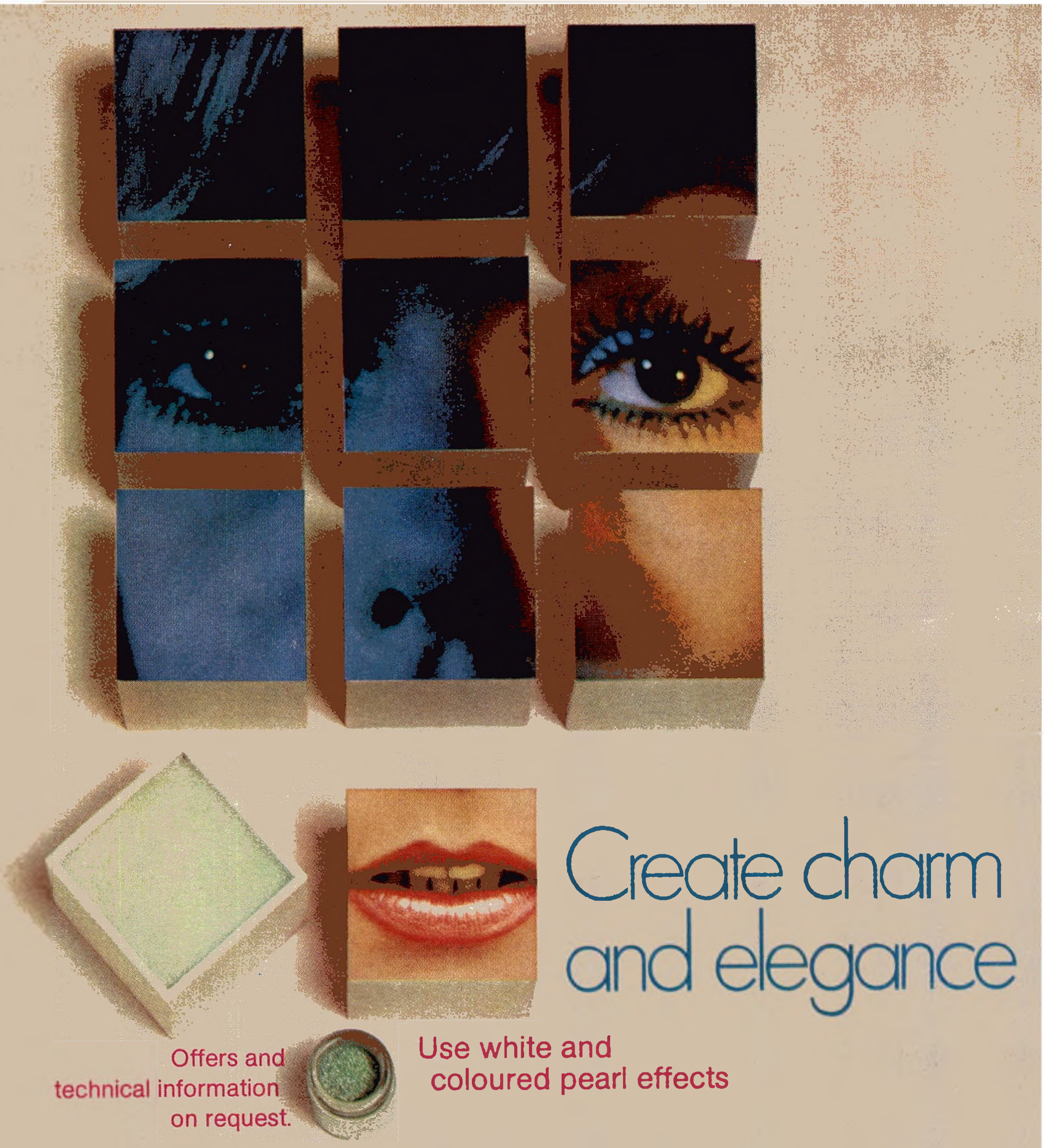
ORIGINAL SCIENTIFIC PAPERS







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Sensory perception and evaluation of hair greasiness: G. C. Dobinson and P. J. Petter. *Journal of the Society of Cosmetic Chemists* **27** 3–14 (1976)

Synopsis—The general principles of sensory evaluation are briefly discussed, with particular reference to the assessment of hair properties in the laboratory. Two procedures are described. The 'meter method' in which assessors place samples on a scale, is rapid, simple to analyse, and most useful for self-contained experiments. The 'ranking method' in which two or more samples are compared at a time, is slower but more sensitive and better suited to intercomparison of experiments using a common standard.

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Instrumental colour assessment—some practical experiences: D. A. Wheeler, D. A. Moyler and J. T. Thirkettle. *Journal of the Society of Cosmetic Chemists* **27** 15–45 (1976)

Synopsis—Instrumental colour assessing techniques promise the cosmetic colour chemist many advantages over the traditional, subjective methods. The authors have examined a range of instruments operating on a variety of principles, including absorption and reflectance spectrophotometry and tristimulus colour space. Practical experience has shown that some of these promises have been fulfilled and that instruments can provide valuable aid to the human colour assessor without being able to replace him entirely. In particular, by providing numerical data on a subjective phenomenon, instruments can increase the speed of colour correction and confidence in the acceptability of a commercial match.

The following papers have been accepted for publication in the *Journal:*

ORIGINAL SCIENTIFIC PAPERS

A study of damaged hair
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Analytical aspects of some classes of risk-bearing substances in cosmetics
D. H. Liem, Dr. Chem.

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Evaluation of flavours in dental creams
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SYNOPSIS FOR CARD INDEXES

A method to evaluate the tube-squeezing properties of toothpaste: BENGT NORÉN. *Journal of the Society of Cosmetic Chemists* **27** 47–61 (1976)

Synopsis—A method has been evolved to evaluate the tube-squeezing properties of toothpaste using a simple inexpensive squeeze device. A toothpaste tube on squeezing shows the rheological properties of a pseudoplastic material. A squeeze equation has been derived and used to estimate the output from a tube under different squeeze conditions to give good correlation with empirical results.

Both toothpaste and tube contribute to the squeeze behaviour of the product and consequently both must be taken into consideration when the product is evaluated.

Examples are given of the changes of squeeze property with storage and the effect of variable gain content and tube dimensions.

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Sensory perception and evaluation of hair greasiness

G. C. DOBINSON* and P. J. PETTER†

Presented at the Symposium on 'A Sensory Approach to Cosmetic Science' organized by the Society of Cosmetic Chemists of Great Britain at Manchester on 7–9th April 1975

Synopsis—The general principles of SENSORY EVALUATION are briefly discussed, with particular reference to the assessment of HAIR properties in the laboratory. Two procedures are described. The 'meter method' in which assessors place samples on a scale, is rapid, simple to analyse, and most useful for self-contained experiments. The 'ranking method' in which two or more samples are compared at a time, is slower but more sensitive and better suited to intercomparison of experiments using a common standard.

The usefulness of sensory testing to the cosmetic chemist is illustrated by a study of hair greasiness, designed to relate sensory assessment of greasiness to the rheological characteristics of the grease. Films of oils, greases and waxes, covering a wide range of CONSISTENCY, were deposited onto hair switches for tactile and visual assessment. For the oils, both tactile and visual greasiness showed a positive linear correlation with the logarithm of viscosity, measured by cone-and-plate viscometer. For the greases and waxes, tactile greasiness was negatively correlated with yield value, measured by cone penetrometer, while visual greasiness showed a maximum in the centre of the consistency range.

INTRODUCTION

Sensory testing is well established in cosmetic science as a means of assessing flavours, fragrances, etc. Its application for the evaluation of physical properties is less well known, particularly in the laboratory where instrumental methods tend to predominate. In fact, it may be that the average cosmetic chemist would tend to regard sensory methods as in-

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herently less reliable than instrumental methods and only to be used where there is no obvious instrumental approach. It is possible, however, for a panel of assessors to function as a useful evaluation tool provided certain conditions are observed. Such a panel can be used not only for assessing complex properties such as 'body' or 'condition' of hair but also as an alternative to an instrumental measurement, for example, of combability.

In this paper we shall briefly review some experimental approaches to sensory testing of hair properties and illustrate with some results obtained from a study of hair greasiness. It is generally convenient, although obviously less realistic, to carry out such evaluations under laboratory conditions using hair switches but, in principle, the methods can be applied *in vivo*.

GENERAL PRINCIPLES OF SENSORY EVALUATION

It is not intended to survey sensory evaluation fully: this topic has been well covered by Harper (1).

In order to use human beings successfully as assessors for evaluation of some property, certain precautions should be taken: the test environment (light, temperature, humidity, etc.) should be kept constant; distractions should be eliminated; assessors in the same panel should be given identical instructions. The number of assessors required depends on several factors amongst which are the required accuracy of the results, the number of test items, the magnitudes of property differences between items and the skill of the judges. As assessors gain experience and confidence, their judgments usually become more consistent. No assessor should observe either the results of another's assessment or how that assessment was obtained.

An assessor can be requested either to indicate the magnitude of some property of a test sample or to rank two or more samples for that property.

When using the former of these alternatives, it is frequently convenient to place each sample on what has been designated as a meter for the test property. This meter, which may be, for example, a length of bench top or a horizontal rod, has no subdivisions and the assessor decides for himself what the range covers. How different assessors might use the meter is indicated in *Fig. 1.* Eight assessors have independently placed four test samples along a designated meter in order to indicate magnitudes of some defined property. This example demonstrates that assessors are using different mental scales (e.g. assessors 4 and 7) and of course do not necessarily agree on the rank order. All assessments, however, can be put on the same

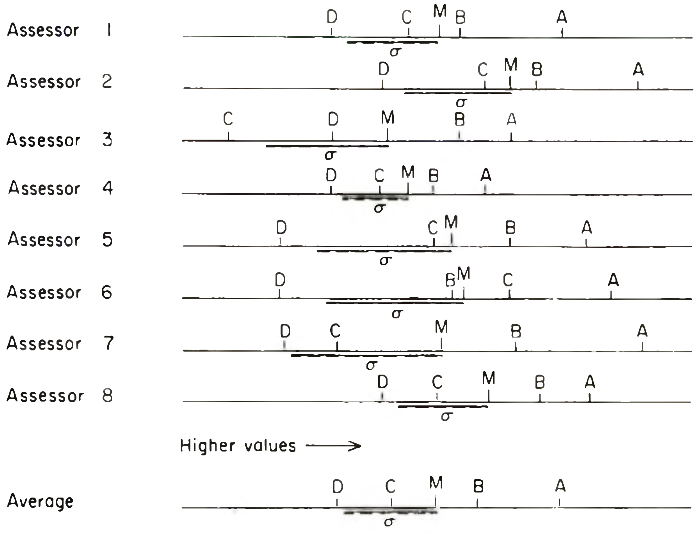

Figure 1. The meter method.

scale by standardizing so that all assessors have the same mean (*M*) and standard deviation (σ). When this is done, all assessments can be averaged together to give an overall assessment in terms of average scale values. This is shown in *Fig. 1.*

The overall rank order obtained is generally found to be reproducible between different panels of assessors, but because individuals use different mental scales both the average scale values and the differences between them are characteristic of the particular panel used. Therefore it is difficult to compare the results of one test with another, even when one common standard is used. For a self-contained experiment, however, this method does have the advantages of speed and simplicity of analysis over the ranking method described below.

An alternative method of investigating property magnitudes uses data in the form of rankings. At least two of the test samples are considered together and the assessor indicates the order of the samples. He will generally go on to rank further sets of test samples, up to a maximum of about ten sets in order to avoid panellist fatigue. It is possible to construct experimental designs which are balanced with respect to such variables as number of replicates and position of samples before the assessor. The design should allow comparisons to be made of samples both of the same type and of different types, so that the variance within each type can be compared to the variance between types. From the ranking data it is possible to generate

Presentation	Ranking	Number
A B C	A B C	2
	A C B	2
	B A C	2
	B C A	1
	C A B	1
	C B A	0
B A D	A B D	3
	A D B	2
	B A D	2
	B D A	1
	D A B	0
	D B A	0
C D A	A C D	3
	A D C	2
	C D A	2
	C A D	1
	D A C	0
	D C A	0
D C B	B C D	2
	B D C	1
	C D B	1
	C B D	2
	D B C	1
	D C B	1
		32

Scale values
M(A) = 0·631
M(B) = 0·072
M(C) = −0·067
M(D) = −0·636

Figure 2. The ranking method.

scale values. Our method uses a generalization by Levitt (2) of the Bradley–Terry model (3) which is based on the assumption that a paired comparison is probabilistic, i.e. for any pair the comparison will not always favour the same item. An example of the results that could be obtained with this method is given in *Fig. 2*, where four samples are examined by eight assessors, each considering four triads. For the purposes of illustration the example is simple; it is quite likely that an experimenter would wish to use, for example, more assessors or more assessments per judge.

There are several advantages of the ranking approach over the meter method, the most important one for the experimenter being that the scale values obtained from one test can be compared directly with the results of another if there is some common standard in each test, since the model gives additive scale values. There are, however, other advantages. Assessors, for example, usually find identifying rank order easier than indicating magnitudes especially where differences are small. There may also be specific reasons for preferring the ranking method as, for example, in the greasiness experiment to be described later, where it was essential to avoid contamination between samples.

APPLICATION OF SENSORY TESTING TO HAIR

In applying sensory testing to the measurement of hair properties, the hair switches used will depend on the properties under study. In this work the test samples were straight switches prepared from European hair so that each switch was 24 cm long by 2 cm wide and contained 0.4 g cm^{-1} of hair along its length. Additional precautions are necessary in order to ensure that error is not introduced into the experimental work because of initial switch differences. The hair to be used should be carefully randomized and cleaned to remove any surface deposits. When the switches have been prepared they should be stored carefully to avoid contamination.

When assessors examine such hair switches—either to rank or estimate property magnitudes—it is usually convenient to hang the switches from a horizontal bar by means of hooks attached to their clamped-root ends.

APPLICATION IN A STUDY OF HAIR GREASINESS

The example we have chosen to illustrate sensory evaluation of hair is taken from a study of the problem of hair greasiness. The factors controlling hair greasiness and its perception are complex, but must include the physical properties of the greasy film of lipid material on the hair surface, and, more specifically, its rheological characteristics. The experiments to be described were aimed at establishing how people's sensory assessment of hair greasiness correlates with the rheological parameters of the grease. Tactile and visual judgments were studied separately, since both modes were believed to be important in the self-assessment of greasiness. While the relevance of rheology to the feel of greasy hair is clear, a possible connection with appearance is perhaps less obvious. However, the most important visual clue to the presence of grease on hair, apart from changes in gloss, is the so-called 'rats-tail' effect, when the hairs tend to adhere together in bundles, and it was this aspect which was studied.

The general plan of the work was to take a number of materials covering a wide range of consistency, from thin mobile oils through greases to solid waxes, to characterize them rheologically and to assess them by sensory testing on hair switches for their greasiness, either tactile or visual. The 11 materials selected are shown in *Table I.* The series began with four silicone oils of increasing viscosity, ranging from a nominal '100 centistokes' up to 'one million centistokes'. Next came semi-solid materials which would normally be thought of as 'greasy': lanolin, petroleum jelly and a high

Table I. Materials selected for greasiness experiments

	Code	Material
Increasing consistency ↓	SIL 1	Poly(dimethylsiloxane) fluids
	SIL 2	
	SIL 3	
	SIL 4	
	LAN	Lanolin
	PJ	Petroleum jelly
	PEG	Poly(ethylene glycol)
	LIP I	Synthetic mixtures of lipid materials
	LIP II	
	LIP III	
	WAX	Paraffin wax

molecular weight poly(ethylene glycol). Mixtures of lipid materials (predominantly oleic and stearic acids and their glycerol esters) were used to span the gap between the greases and the relatively hard paraffin wax.

These materials were applied to hair switches by spraying 1% w/w solutions in ether from pressurized aerosol packs. Each switch was sprayed until the deposit equalled 1% of the weight of the hair (this being typical of the grease levels found on hair *in vivo*) and finally the hair was combed through to promote uniform distribution. (Preliminary experiments showed that this combing step did not remove a significant amount of material from the switch.) Materials were compared three at a time in a series of sensory tests, linked together by including each time one material common to the previous group. In this way, the complete body of data could be analysed together to give an overall picture, placing all 11 materials on a scale of relative greasiness.

The sensory assessments were carried out according to the general ranking procedure already described. Tactile and visual assessments were carried out separately. In the tactile test, switches were presented for ranking in pairs, hanging behind a screen so that the panellists could feel but not see them (*Fig. 3*). In order to avoid transfer of material between switches, panellists were asked to feel one switch in each hand, and to wash their hands between each pair. Six switches were used for each test, made up of duplicates for each of the three materials being compared. Twelve panellists each assessed six pairs, in the course of which every switch was felt twice, once in the left hand and once in the right, in order to take account of any bias.

In the visual test, panellists could see the switches but were not allowed

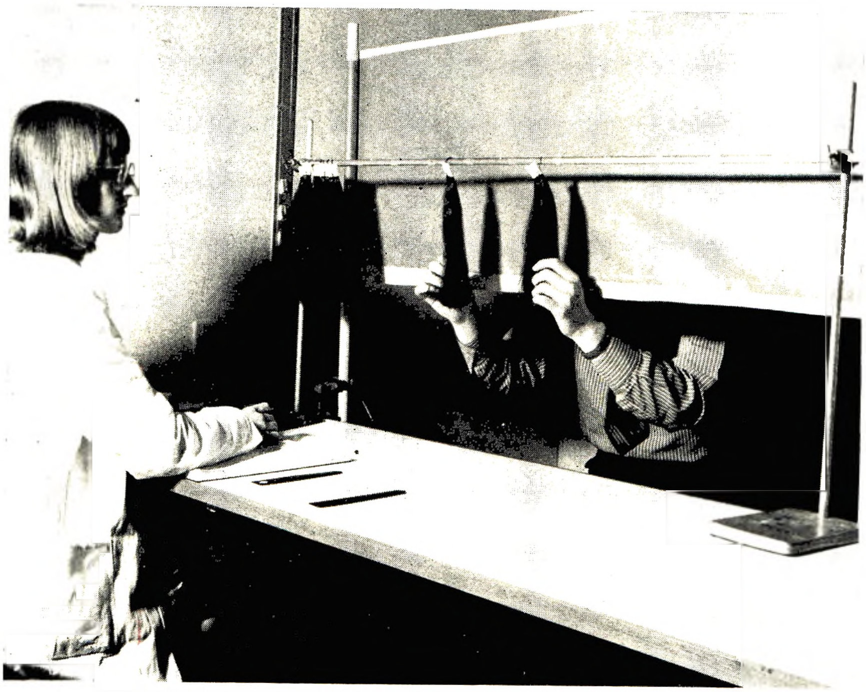

Figure 3. Tactile assessment of greasiness.

to touch them. Lighting conditions were chosen to avoid highlights on the hair, so that gloss variations were not visible and the predominant visual cue to greasiness was the 'rats-tails' effect. The test design was similar to that for the tactile assessment, except that the panellists ranked three switches at a time.

By analysis of the data from these tests in the way described earlier, it was possible to assign numerical values to each of the eleven materials on a scale of greasiness, either tactile or visual. If these scale values are considered in relation to the subjective order of consistency of the materials, a general pattern begins to emerge (*Fig. 4*). We see that the tactile greasiness is low for the thinner oils, increases to a maximum with the semi-solids, and decreases again as the materials become harder and waxier. The visual greasiness pattern, on the other hand, is more complex, and it is interesting that over part of the range (LAN to LIP II) the visual greasiness appears to increase with consistency at the same time as the tactile greasiness is decreasing.

These relationships became clearer when the rheological characteristics of the materials were quantified instrumentally. Over such a wide range of materials, no single rheological parameter can serve as the basis for comparison, but it was found possible to use a minimum of two parameters. The oils were characterized by viscosity measurement with a Ferranti–Shirley cone-and-plate viscometer, while for the solids and semi-solids a

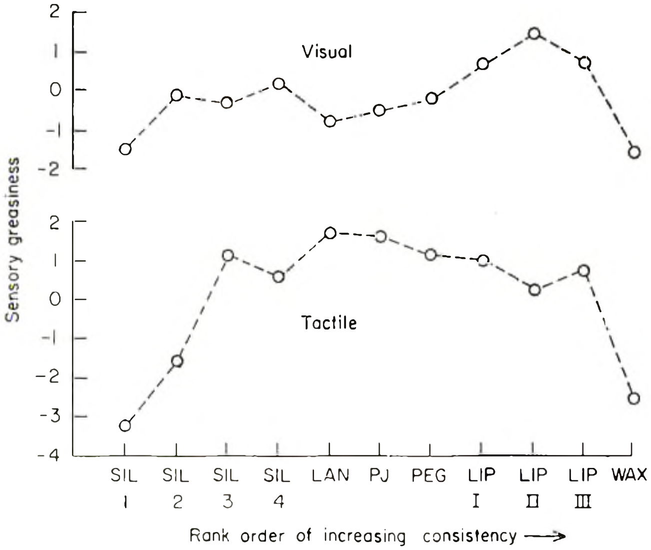

Figure 4. Sensory greasiness *vs* subjective consistency.

cone penetrometer was used to measure the yield value (i.e. the minimum stress below which the material ceases to flow). Both of these are standard techniques to be found in most rheological textbooks (e.g. Sherman (4)), and need be described only briefly here.

The cone-and-plate viscometer (*Fig. 5*) consists essentially of a slightly conical disc rotating with its apex just touching a flat stationary plate. The fluid sample is contained in the gap between cone and plate, and the torque, G, on the cone can be measured at any rotational speed, Ω. It can be shown that the shear rate is constant throughout the sample and that the dynamic viscosity, η, is given by:

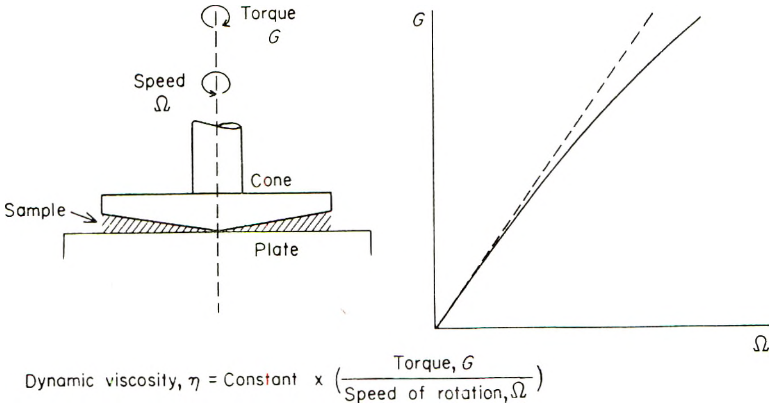

Figure 5. Ferranti cone-and-plate viscometer.

$$\eta = \frac{KG}{\Omega}$$

where K is a constant depending only on the geometry of the cone. The plot of G versus Ω was a straight line for the thinnest silicone oil, but became increasingly curved for the remaining three and in these cases the 'low shear' viscosity was calculated from the initial slope.

The cone penetrometer (*Fig. 6*) is a standard instrument for characterizing fats and greases, and the method used to obtain yield values from penetration measurements was that described by Haighton (5). In this instrument, a cone, of weight W, penetrates under gravity the flat surface of the sample in a cylindrical cup. As penetration proceeds, the shear stress

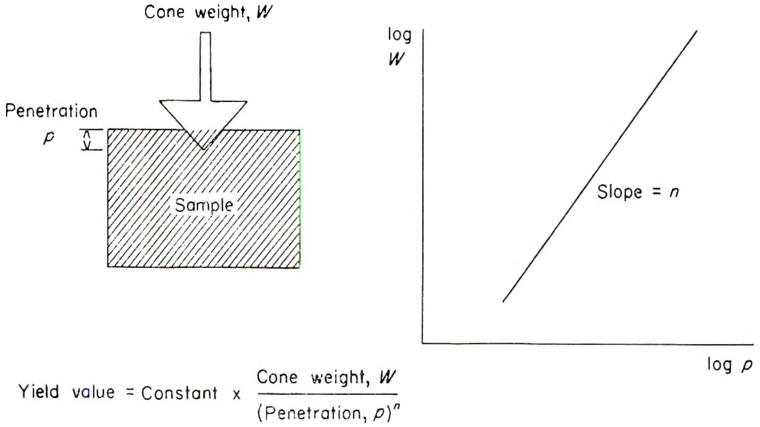

Figure 6. Cone penetrometer.

decreases until it reaches a value just balanced by the rheological stability of the sample, and the cone ceases to move. From this equilibrium penetration, p, the yield value may be calculated as

$$\text{yield value} = \frac{k\,W}{p^n}$$

where k is a constant depending on the cone angle and is tabulated by Haighton. The value of n is approximately 2, and may be found by loading the cone to various weights, plotting log W against log p and determining the slope of the line. In this work, n was found to have an average value of 1.79.

The results of these two rheological measurements are given in *Table II.* The yield value quoted for paraffin wax is an approximate figure, since the penetrometer was not really suitable for such a hard material, and the penetration was too small to measure accurately. It was not practicable to carry out these measurements at a temperature other than 25°C, although it is recognized that this is not identical to the temperature of the materials during sensory assessment: the visual assessments were carried out at room temperature (22°C) while in the tactile assessments the films must have been at some temperature between room and body temperatures.

Let us now consider again the sensory test results in relation to these values. First, for the silicone oils (*Fig. 7*), plots of sensory greasiness against

Table II. Rheological characteristics of materials

Material	Viscosity (Nsm^{-2})	Yield value (kNm^{-2})
SIL 1	0.114	
SIL 2	25.5	
SIL 3	50.5	
SIL 4	302	
LAN		1.13
PJ		1.40
PEG		3.47
LIP I		6.39
LIP II		14.6
LIP III		34.5
WAX		~7000

the logarithm of the viscosity suggest a straight line relationship for both tactile and visual assessment, although one would clearly like to have more data points. This type of logarithmic relationship between stimulus and sensory response is, of course, common throughout psychophysics (1).

For the remaining materials (*Fig. 8*), there is evidence of a linear relationship between tactile greasiness and the logarithm of the yield value, but in this case, as we have already noted, the greasiness decreases with increasing consistency. Other workers have found the yield value of semi-solid materials

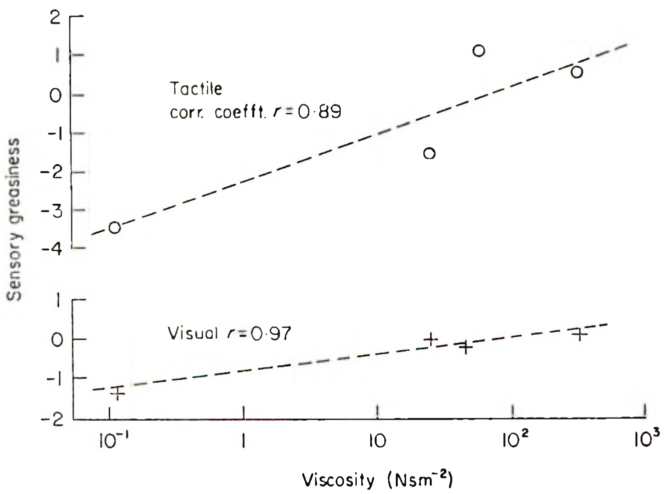

Figure 7. Sensory and instrumental measurements for silicone oils.

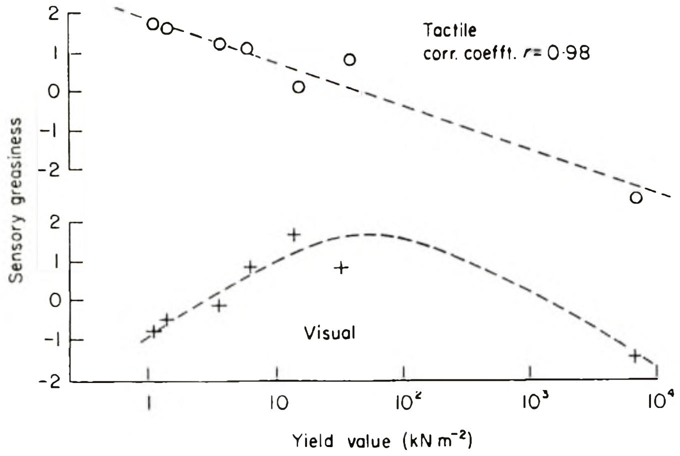

Figure 8. Sensory and instrumental measurements for greases and waxes.

important in determining the sensory assessment of the consistency of skin creams (Suzuki and Watanabe (6)) and the ease of application to the skin (Barry and Grace (7)). The relationship for visual greasiness is obviously more complex than that for tactile greasiness. The increase with increasing yield value over the lower half of the range probably reflects the increasing tendency of the hairs to adhere together to form 'rats-tails', with the ease of separation of the hairs inversely related to the yield value. It seems reasonable, however, that eventually the curve will turn down again in the hard, waxy region, as indicated by our result for paraffin wax.

Although more work is required before the physical basis of the perception of hair greasiness can be fully understood, these results suffice to demonstrate that it is possible to obtain quantitative measurements of hair greasiness by means of sensory assessment. Moreover, our work on hair switches could, in principle, be extended to assessment *in vivo*, comparing the greasiness of real heads, although so far we have made only a few preliminary experiments in this direction. Finally, we would emphasize again that greasiness is just one example of a property which can be evaluated by sensory testing. We have successfully applied the technique to a wide range of hair properties, including, for example, combability, gloss, softness and 'fly-away', and the sensory approach is particularly useful for properties which have no obvious physical correlate that can be measured instrumentally.

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Instrumental colour assessment— Some practical experiences

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Presented at the Symposium on 'A Sensory Approach to Cosmetic Science' organized by the Society of Cosmetic Chemists of Great Britain at Manchester on 7–9th April 1975

Synopsis—INSTRUMENTAL COLOUR ASSESSING techniques promise the cosmetic colour chemist many advantages over the traditional, subjective methods. The authors have examined a range of INSTRUMENTS operating on a variety of principles, including ABSORPTION and REFLECTANCE SPECTROPHOTOMETRY and TRI-STIMULUS COLOUR SPACE. Practical experience has shown that some of these promises have been fulfilled and that instruments can provide valuable aid to the human colour assessor without being able to replace him entirely. In particular, by providing numerical data on a subjective phenomenon, instruments can increase the speed of colour correction and confidence in the acceptability of a commercial match.

INTRODUCTION

Of all the human senses, the phenomenon of colour vision is the one which has yielded up its secrets most readily to patient scientific examination. Whilst it would be an exaggeration, even today, to say that we understand all aspects of colour vision, sufficient was known about the human response to light stimuli by 1925 to enable purely instrumental 'measurement' of colours to be made.

Instrumental colour assessment was pioneered largely by textile and paint companies and since those early days such techniques have gained

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widespread acceptance in these and other industries where colour plays an important role. A notable exception appears to be the cosmetics industry which, whilst being aware of these developments, has been unable—or unwilling—to put them to its own use.

The value of instrumental colour evaluation is determined by the extent to which it fulfils in practice a number of clear, theoretical advantages over assessment by human observation. Some of the more important of these (which are claimed to different extents by the various techniques available) can be summarized as follows.

Qualitative

The assessment obtained for a given colour or colour difference is consistent and reproducible to a high level of approximation. It does not vary with time, or with the identity or the physical or mental condition of the operator and is not subject to his human bias. This allows physical standards to be replaced by invariable instrumental parameters and close, consistent agreement to be reached between different personnel or laboratories. Such parameters may be used as part of an unambiguous specification as, for example, between supplier and user or for the purposes of laboratory test procedures such as fade and storage testing.

Quantitative

It is often possible to establish a quantitative or semi-quantitative relationship between the concentration of the various components of a product and its resulting colour as measured by the instrument. This enables instrumental parameters to be used to predict the correction required to obtain a match to standard and in some cases, to predict the combination and concentration of available colourants which will formulate a new desired colour.

Economic

Instruments need no training themselves and their operators usually very little. They can be used by non-specialist laboratory or factory personnel with little problem. It can often be argued that it is cheaper, in the long term, to instal and maintain a suitable 'colour-measuring' instrument than to train and maintain specialist colour technicians or chemists.

Since 1971, one or more of the authors have been engaged in investigating the extent to which these promises are fulfilled in practice when applied to cosmetic materials and products. Whilst it is true that the list of techniques and apparatus investigated is far from exhaustive and the extent to which they have been tested far from complete, it is the authors' belief that the experiences which are reported here might prove interesting to those who are concerned with colour assessment in the cosmetics industry.

USE OF AN ABSORPTION SPECTROPHOTOMETER FOR COLOUR MATCHING CLEAR, COLOURED, LIQUID PRODUCTS

It is a common observation that two coloured solutions are indistinguishable if they are composed of identical solvents and dyes in identical concentrations. This applies no matter how many dyes are used to produce the colour. In such cases, therefore, colour matching resolves itself into the problem of incorporating into the sample, the same dyes in the same concentration as in the colour standard. The human operator attempts this by subjective assessment, but the modern spectrophotometer represents a means of measuring the concentrations of substances in solution with great accuracy and precision and therefore commands considerable advantages in speed and accuracy—particularly in dealing with colours produced by two or more dyes (which are very difficult to handle for the human operator). The measured parameter, absorbance (A) is linearly related to the concentration of a light absorbing species (C) and the path length of the light through the solution (L) by the familiar Beer–Lambert equation:

$$A = KCL$$

where K is a statistical probability factor (the absorption coefficient). This equation holds true for a given light absorbing species at a specified wavelength.

The first benefit to be expected from absorption measurements is a simple means of checking each fresh delivery of soluble dye for purity. *Table I* relates to four deliveries of the same dye. The absorbances obtained for a standard concentration of each—which would be identical for pure dyes—are given in the second column, whilst the third column indicates the relative purity of each delivery (delivery one being used as standard).

In our laboratory, each delivery of dye is checked and associated with a correction factor by which the formula quantity of dye is multiplied so

Table I. Absorbances at 625 nm of 4 batches of F D & C Blue No. 1 (Concentration $5.0 \times 10^{-4}\%$ w/v)

Batch	Absorbance	Relative purity
1	0.726	100.0
2	0.699	96.4
3	0.688	94.8
4	0.693	95.5

as to compensate for dye purity in the production process. Should the batch need subsequent correction, the following actual examples will illustrate the process.

For practical purposes, the absorption coefficient is expressed in terms of the so-called *E* one-one (E^1_1), this being the (imaginary) absorbance of a 1% solution of the absorbing species in a cell of 1 cm thickness.

Example 1—Spectral match, single colour

Product	Cologne
Composition	Perfume base + blue dye
Wavelength of maximum absorption of dye	625 nm
Absorbance of standard at 625 nm	0.224 units
Absorbance of sample at 625 nm	0.186 units
E^1_1 of dye at 625 nm	1172.1 units
Visual assessment	Sample weak in blue and in yellow
Problem	How much dye must be added to a 450-litre batch to obtain a match?

Required increase in absorbance = 0.224 − 0.186 = 0.038 units.

Since a 1 % concentration increase would give a change of 1172.1 units, the required increase is:

$$1 \times \frac{0.038}{1172.1} = 3.24 \times 10^{-5}\%.$$

To increase the concentration of dye by this amount in 450 litres requires: $3.24 \times 10^{-5} \times 4.5 \times 10^{3} = 0.1458$ g.

Result: The addition of 0.146 g of dye gave an absorbance of 0.226 units

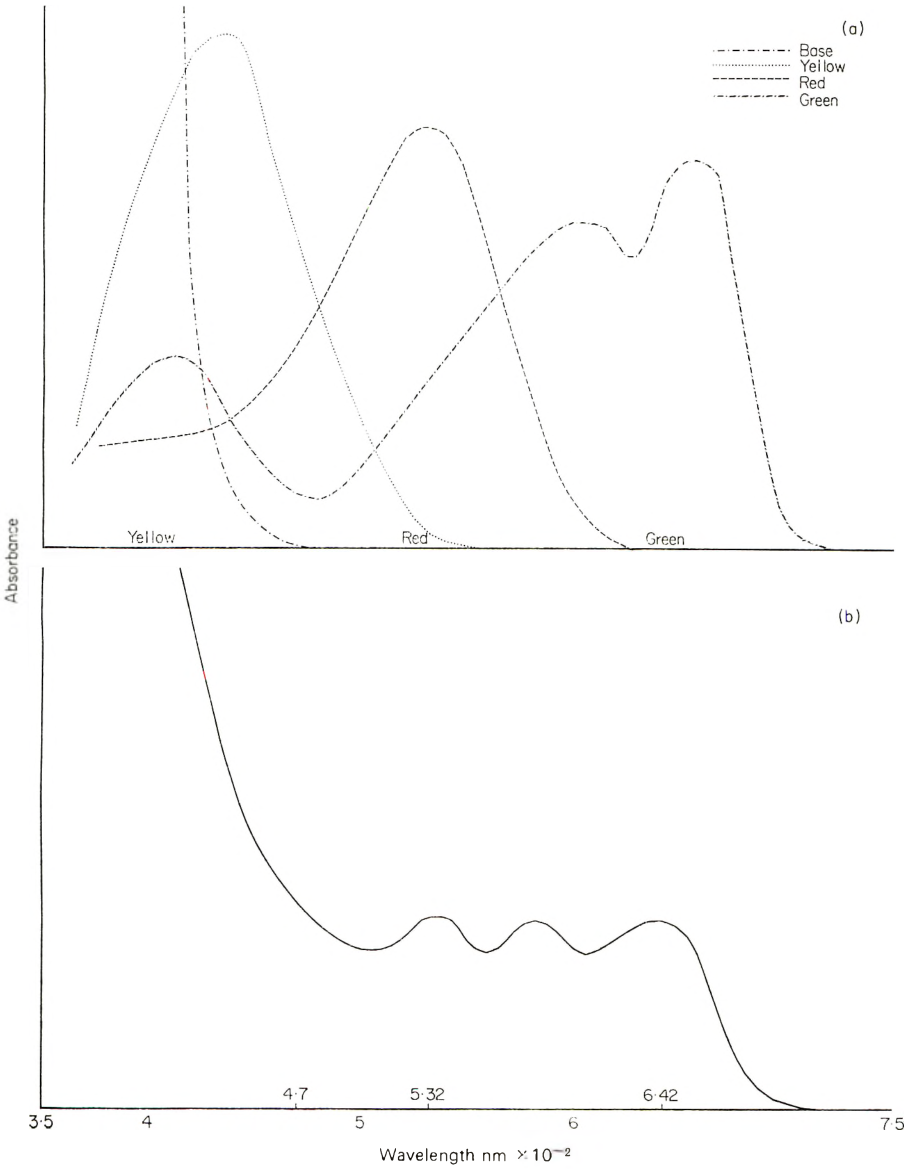


Figure 1(a). Absorption spectra of aftershave components. (b) Absorption spectrum of an aftershave.

> at 625 nm. Visual assessment was a good match in blue, but sample still slightly weak in yellow. We concluded that the physical standard had 'yellowed' with age.

If we accept that the perfume base plus its various additives will inevitably get darker with age, there seems nothing for it but to abandon 'real' colour standards in favour of stable metameric substitutes, or to define the colour standard in terms of instrumental readings. We have adopted the latter with some success.

The absorption spectra of multi-dye products are obtained simply by adding together the spectra of the individual dyes at their relevant concentrations. In other words, the absorbance at any wavelength of the final product will be

$$A_{\lambda 1} = K_{\lambda 1}CL + K^{1}_{\lambda 1}C^{1}L + K^{11}_{\lambda 1}C^{11}L + \ldots\ldots\ldots\ldots$$

where K, K^1, K^{11} and C, C^1, C^{11} refer to individual dyes. At another wavelength λ_2

$$A_{\lambda 2} = K_{\lambda 2}CL + K^{1}_{\lambda 2}C^{1}L + K^{11}_{\lambda 2}C^{11}L + \ldots\ldots\ldots\ldots$$

Fig. 1(a) and *1(b)* illustrate this additive phenomenon. The absorption spectrum of an aftershave product is obtained by the algebraic addition of the spectra of three dyes in suitable concentrations plus a contribution from the perfume base. Three measurements are taken at points on the spectrum where the absorbance is predominantly due to each of the controllable variables—one each at the maxima of the red and green components (532 and 642.5 nm, respectively) together with a point on the yellow curve where the absorption by the base does not interfere (470 nm).

Example 2—Spectral match, three colours

Product	Aftershave lotion
Composition	Perfume base plus three dyes; red, green, yellow
Wavelengths of maximum absorption of dyes: red	532 nm
green	642.5 nm
yellow	425 nm (measured at 470 nm)

Absorbance of standard at			
532 nm	0.152 units		
642.5 nm	0.140 units		
470 nm	0.314 units		
E^1_1 of dyes	470 nm	532 nm	642.5 nm
Red	183.9	507.8	—
Green	22.9	49.7	176.4
Yellow	445.5	14.7	—
Problem	What concentration of dyes having the above E^1_1 values would be needed to match the standard?		

At 470 nm,

absorbance $0.314 = (183.9\ C_r) + (22.9\ C_g) + (445.5\ C_y)$

At 532 nm

absorbance $0.152 = (507.8\ C_r) + (49.7\ C_g) + (14.7\ C_y)$

At 642 nm

absorbance $0.140 = (176.4\ C_g)$.

Where C_r, C_g and C_y are the concentrations, expressed in percent, of the red, green and yellow dyes respectively.

From these simultaneous equations.

$$C_g = 7.936 \times 10^{-4}\%\ wv^{-1}$$
$$C_r = 2.048 \times 10^{-4}\%\ wv^{-1}$$
$$C_y = 5.794 \times 10^{-4}\%\ wv^{-1}$$

Result: A trial 10-litre batch of aftershave was made incorporating the above concentration of dyes.

Absorbance at 470 nm = 0.305 units
532 nm = 0.157 units
642.5 nm = 0.141 units

Visual assessment: a very good match.

Three-component colour matching problems such as this pose considerable difficulties for the unaided human assessor. The introduction of this simple instrumental procedure dramatically reduced the correction time for this product at our factory.

The assessment of the purity of soluble dyes and their concentrations in clear liquid products by spectrophotometer has been practised for a number of years in the authors' laboratory with considerable success. In practice, each batch of product is arranged to be slightly too strong in colour so that a single correction can be calculated involving the addition of solvent; this takes care of any slight manufacturing variations which, it seems, are impossible to eliminate completely.

REFLECTANCE SPECTROPHOTOMETRY

Having achieved success in dealing with clear, coloured, liquid products, we were anxious to test the spectrophotometer's performance in the assessment of coloured solids and opaque liquids. For this we required a reflectance attachment which modifies the light-path through the instrument so as to allow the examination of light reflected from the surface of the sample rather than that passing through it. Several designs of reflectance device were tried and that finally chosen was of the integrating sphere variety, since this showed less variation of output with sample orientation than did any of the others, especially for pearly products. *Fig. 2* illustrates the form in which data is obtained from a reflectance spectrophotometer. The reflectance curves A, B, C and D were obtained from lipstick components and represent a measure of the percentage of incident light which was reflected at each wavelength for each component.

It can easily be seen that the pigments A and B reflect mainly in the red region (A being more orange than B). D reflects light over most of the

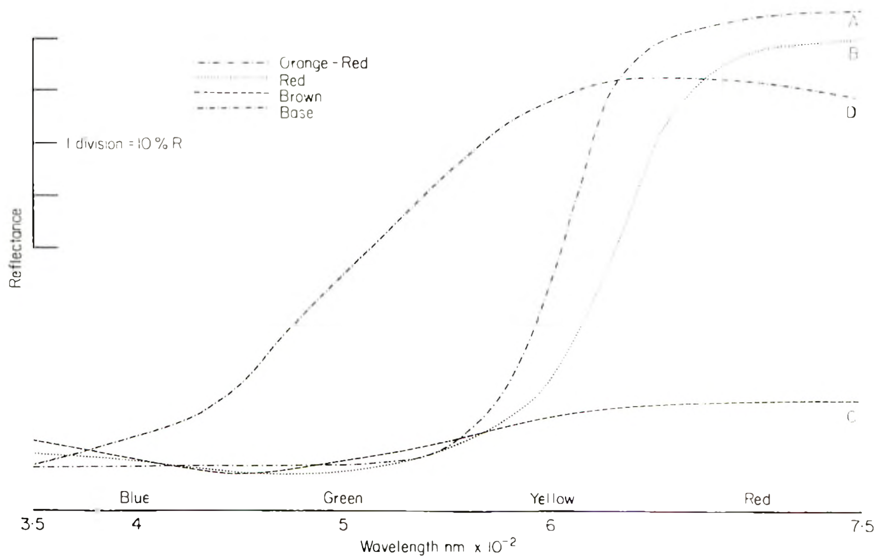


Figure 2. Reflectance spectra of lipstick components.

visible spectrum and is yellow in appearance whilst C is not a good reflector, but absorbs less in the red and orange regions and is therefore dark brown in colour.

Although there is a simple quantitative relationship between the concentration of a colour and its percentage reflectance at a given wavelength (as in absorption spectrophotometry) we soon found that the combinations of similar dyes and the relatively large number of components contributing to the colour of the final solid product made any simple quantitative treatment of colour correction both time consuming, and imprecise when the instrument was used in the reflectance mode. Moreover, the amount and quality of light reflected from a surface depends not only on the colour of the individual components but also upon their distribution and particle size as well as the depth of gloss and refractive index of the surface itself. Nevertheless, we were interested to discover to what extent discernible differences in the observed colour of two similar products were mirrored by their reflectance spectra—in the hope that such data could be used as invariable standards.

Fig. 3 illustrates the spectra of two samples of the same shade of lipstick. The samples were prepared by melting the lipstick into a 27 mm godet and flaming the surface to a smooth, even finish. Curve A was obtained from

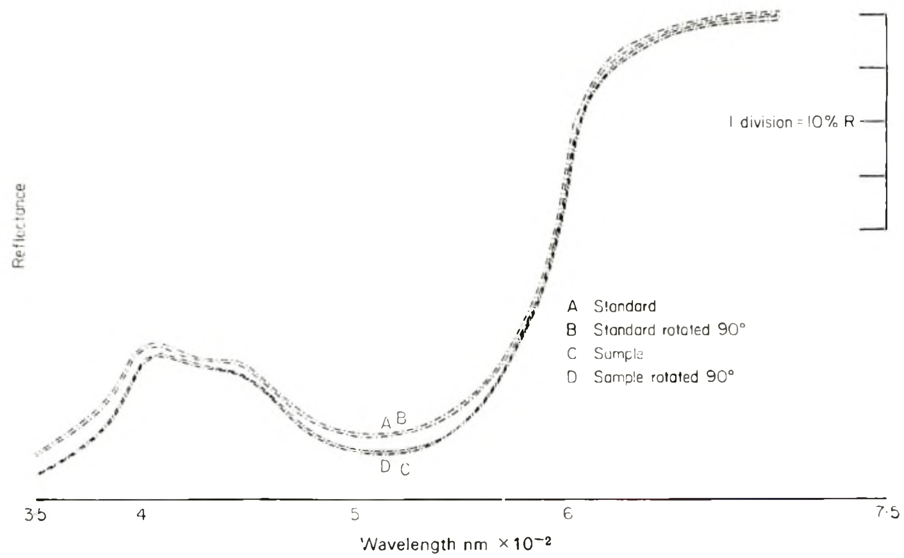


Figure 3. Reflectance spectra of a lipstick.

the standard material and B from the same sample after having rotated the godet through 90° in the same plane. It will be noticed that the two curves are not precisely coincident. Curves C and D were similarly obtained from another batch of the same lipstick shade which was judged by visual assessment to be 'slightly blue to standard and on the borderline of acceptability'. In *Fig. 4*, the 'blue' end of these four curves have been scale expanded; it seems fairly clear from this figure that the second batch reflected marginally less than did the standard at the blue end of the spectrum.

These results were typical of those obtained from pressed powders, gels and creams as well as lipsticks and seemed to indicate that differences in reflectance spectra for samples showing visually detectable colour differences could be larger than errors due to sample preparation and presentation. This was most encouraging, but it was still not clear how this information could be used to help in the process of colour correction.

Table II sets out the successive colour corrections (made by visual assessment only) of a particularly troublesome batch of face powder from first makings to final match. In all, five corrections were made and the consequent colour changes were monitored by the reflectance spectrophotometer in the differential mode. In this manner of use, the standard white surface which normally functions as the 100% reference for the instrument

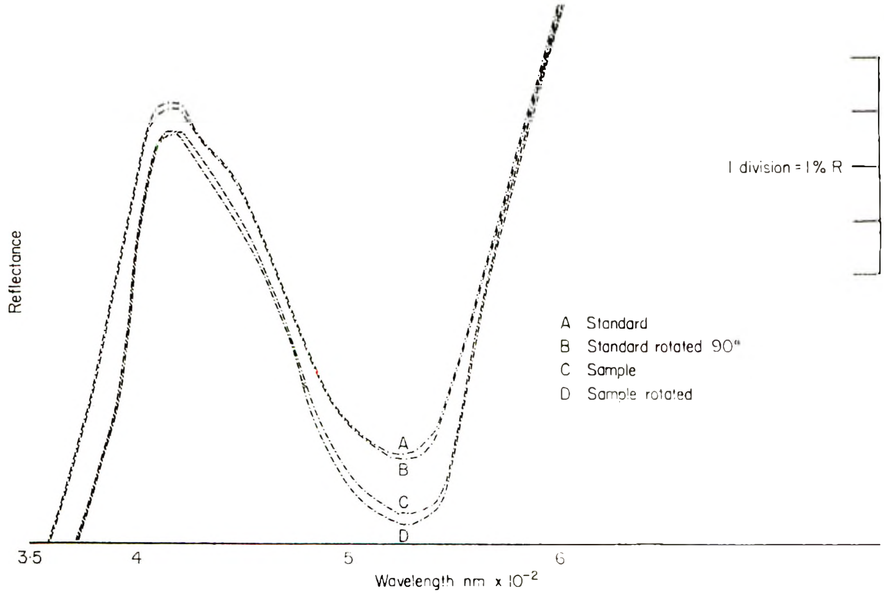


Figure 4. Reflectance spectra of a lipstick.

is replaced by a standard sample of the product to be matched: thus the spectrum actually recorded represents the difference in reflecting power between the standard and sample product at each wavelength. For an absolutely perfect match, the spectrum would be (theoretically) a straight line parallel with the wavelength axis.

Table II. Face powder corrections

	Correction
1st Sample	+Brown+Yellow
2nd Sample	+Brown
3rd Sample	+Base+Yellow
4th Sample	+Brown+Yellow
5th Sample	+Yellow
6th Sample	Correct

Curve A in *Fig. 5(a)* represents the difference between the starting material and the standard colour. It shows the sample to be deficient in the yellow and red wavelengths.

Curve B shows that the first correction resulted in over compensation at these wavelengths whilst the blue end of the spectrum is relatively unaffected. The effect of adding brown (2nd correction, Curve C) was needed to compensate for the previous overcorrection, but now the colour was too intense overall. The addition of base and yellow (3rd correction, Curve D) results in the relative lightening of the colour throughout the spectrum. The final adjustments (Curves E and F in *Fig. 5(b)*) are comparatively minor, but note that the final match is far from a straight line.

Thus it can be seen that the reflectance spectra obtained during the course of a colour correction were capable of a meaningful interpretation and were consistent with the visual colour changes produced. How to use these data to provide accurately predicted colour corrections in terms of precise additions of the various pigments was not clear, however. The spectra took some time to produce and their interpretation was not easy. It would be far easier if the data could be presented in some form which made the connection with real visual sensations more obvious. Thus we were led to consider the use of tristimulus colour space—a concept which developed because of the remarkably simple way in which the eye and brain seem to combine to give subjective colour sensations in response to visible light stimuli. We were concious that this step led us simultaneously closer to true instrumental colour assessment but away from any precise relationship between the measured instrumental parameters and the concentration of coloured components contributing to the final colour of the product.

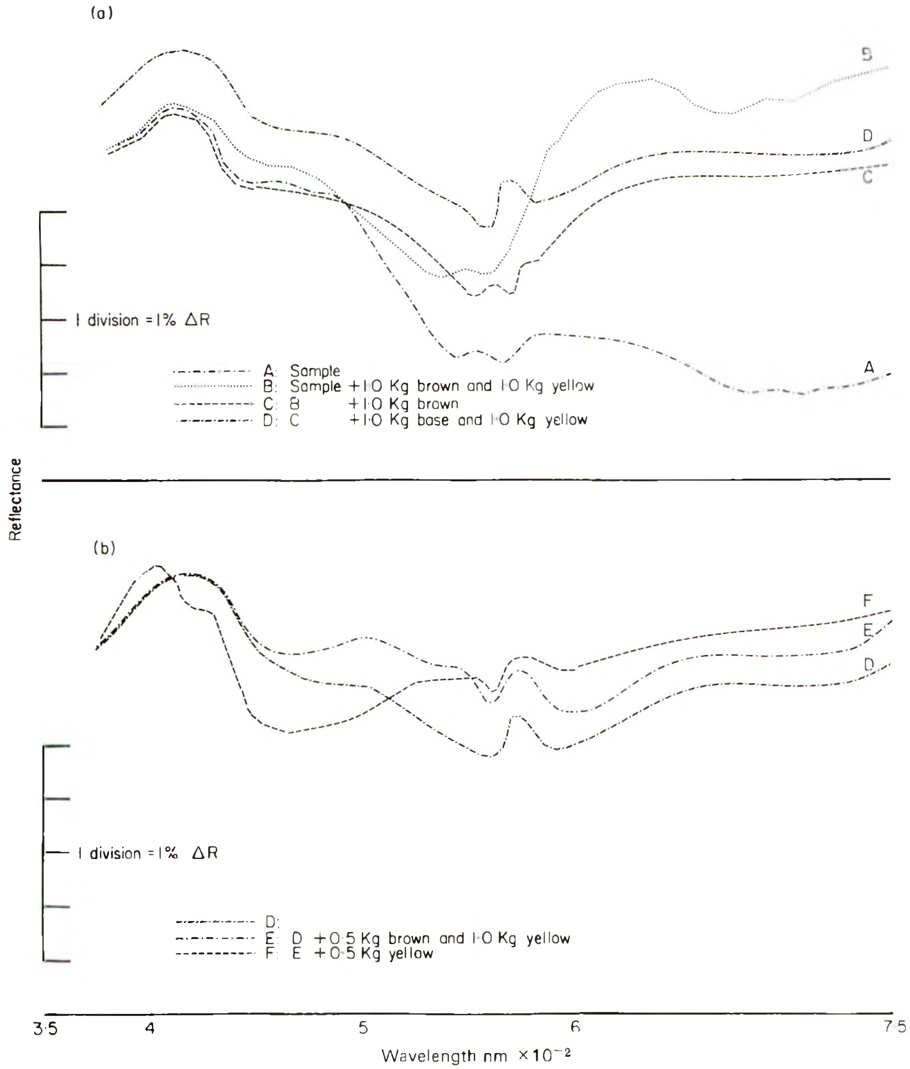


Figure 5. Differential reflectance spectra of a face powder.

Our first undertaking was to integrate some of our reflectance curves in order to obtain the well-known CIE tristimulus values X, Y, Z, thus:

$$X = \sum_{400}^{700} E(\lambda).R(\lambda).\bar{x}(\lambda)$$

$$Y = \sum_{400}^{700} E(\lambda).R(\lambda).\bar{y}(\lambda)$$

$$Z = \sum_{400}^{700} E(\lambda).R(\lambda).\bar{z}(\lambda)$$

Where light having energy $E(\lambda)$ is incident upon a surface having reflectance $R(\lambda)$ and $\bar{x}$, $\bar{y}$, $\bar{z}$ are the CIE spectral distribution curves for normal vision. These tristimulus values locate the colour as a point in colour space and we found invariably that the location so calculated was consistent with the colour measured. However, the task of performing the calculation was formidable and had to be given to our computer. We then examined a number of 'abridged spectrophotometers' which function by replacing the usual prism or grating by filters designed to correspond to the three CIE spectral distribution curves and so measure X, Y and Z directly.

Thus having simplified the procedure for plotting the position of objects in colour space, we began to compute the small differences between co-ordinates of standard and corresponding production samples for various products. We found that even the smallest visually perceptible colour difference was detectable by the spectrophotometer, but that the exact interpretation of such differences and the assessment of what ought to be done to reduce them was difficult. There were two reasons for this:

Without an accurate coloured model of CIE colour space, two sets of co-ordinates give very little indication of the nature of the visual colour difference between them.

CIE colour space is not uniform with respect to just perceptible colour differences. The eye, for example, detects a far greater colour difference for a given co-ordinate difference in the blue region than for the same co-ordinate difference in the green region.

Fortunately, these two difficulties have long been recognized by workers who, like us, felt the need for 'appearance scales' rather than the 'colour-specifying scales' of the CIE. Alternatives to the CIE system, known as Uniform Colour Scales, began to appear soon after the adoption of the CIE Standard Observer data. Designers of UCS systems transformed these data by means of equations in order to create scales having the following desirable properties:

They distorted CIE colour space so as to give more uniform visual colour differences for similar co-ordinate differences.

They were readily understandable, usable and relatable to visually recognized attributes of object colour appearance.

They remained capable of being measured by instrumental techniques.

Many such scales have been created, none of them perfect. The one which appealed to us, however, was developed in 1958 by Richard Hunter in the USA (1). The Hunter Uniform Colour Scales consist of two chromaticity co-ordinates, *a* and *b* and a lightness dimension, *L*. They are obtained from the CIE co-ordinates via the following equations:

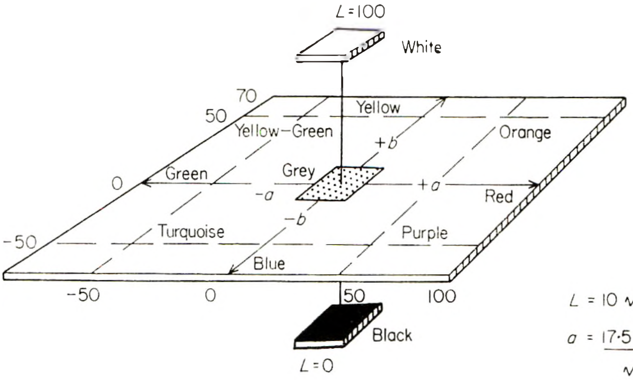
$$L = 10\sqrt{Y} \qquad a = \frac{175\,(X_{\%} - Y)}{L} \qquad b = \frac{70\,(Y - Z_{\%})}{L}$$

$$(X_{\%} = 1.02X \qquad Z_{\%} = 0.847Z)$$

These equations arise quite naturally from the observed facts that more uniform colour space can be obtained on expanding X–Y differences by a factor of 2.5 relative to Z–Y differences and that when measuring lightness, there is an approximately square root relationship between our subjective response and the amount of energy actually reaching the eye. In addition, the '*a*' and '*b*' chromaticity dimensions need to be expanded by a factor of 7 to bring them to the same level as the lightness function, '*L*', so that the units on all three scales represent approximately equivalent degrees of visual difference.

Besides the greater uniformity which it displays, *L*, *a*, *b* colour space enjoys the enormous advantage of being an opponent colour system. This is illustrated in *Fig. 6* where it can be seen that the central region of *L*, *a*, *b* colour space is a neutral grey. Movement along the '*a*' axis leads progressively to pure red in one direction and to pure green in the other. Similarly, the '*b*' axis represents a yellow to blue transition. The '*L*' axis leads from neutral white at 100 to neutral black at zero. It will be clear immediately that the co-ordinates $L = 63.5$, $a = +11.9$, $b = +35.3$ refer to a light, reddish-yellow and that a second set of co-ordinates $L = 61.7$, $a = +12.3$, $b = +35.3$ refers to a related colour which is slightly darker and more red. This represents a considerable improvement in ease of interpretation over unmodified CIE colour co-ordinates.

Proof that the third criterion of useful UCS design is met by the *L*, *a*, *b* system is provided by the existence of the Hunterlab D25 Tristimulus



$$L = 10\sqrt{Y}$$

$$a = \frac{17{\cdot}5\,(1{\cdot}02\,X - Y)}{\sqrt{Y}}$$

$$b = \frac{7\,(Y - 0{\cdot}847\,Z)}{\sqrt{Y}}$$

Figure 6. The *L*, *a*, *b* colour solid.

Colorimeter which gives rapid and direct read-out of both X, Y, Z and L, a, b co-ordinates on any sample. This instrument can examine reflected or transmitted light through separate photodetectors equipped with tristimulus filters. The signals are fed into a measuring unit where X, Y and Z are generated as voltages and fed to a digital voltmeter display. The L, a, b co-ordinates are generated by printed circuits from the X, Y, Z voltages and may be alternatively displayed at the touch of a button.

This instrument produced interesting results in our laboratory almost from the moment it was installed. Our preliminary experiment consisted of monitoring the effect of grinding increasing amounts of three common oxide pigments into pure talc. The results are illustrated in *Fig. 7(a)–(c)*. From *Fig. 7(a)* it can be seen that all three oxides increased the value of '*a*' and that all the '*a*' values were positive; we concluded that the yellow oxide was a reddish-yellow and that the brown was a reddish-brown. This agreed with visual assessment. Naturally, the red oxide increased the '*a*' value the most and, as expected, the '*a*' co-ordinate reached a maximum value in each case. What was not expected, however, was the rapidity with which the maximum value was reached. It is clear from the curve that the maximum hue intensity is reached with a concentration of less than 5%. This is mirrored in *Fig. 7(b)* which relates to the yellow-blue co-ordinate, '*b*'. All '*b*' values were positive (indicating that the brown and red had a yellow tone in them) and in each case the maximum hue was reached at a concentration of about 5%.

Fig. 7(c), which shows the trend of the lightness dimension, '*L*', is

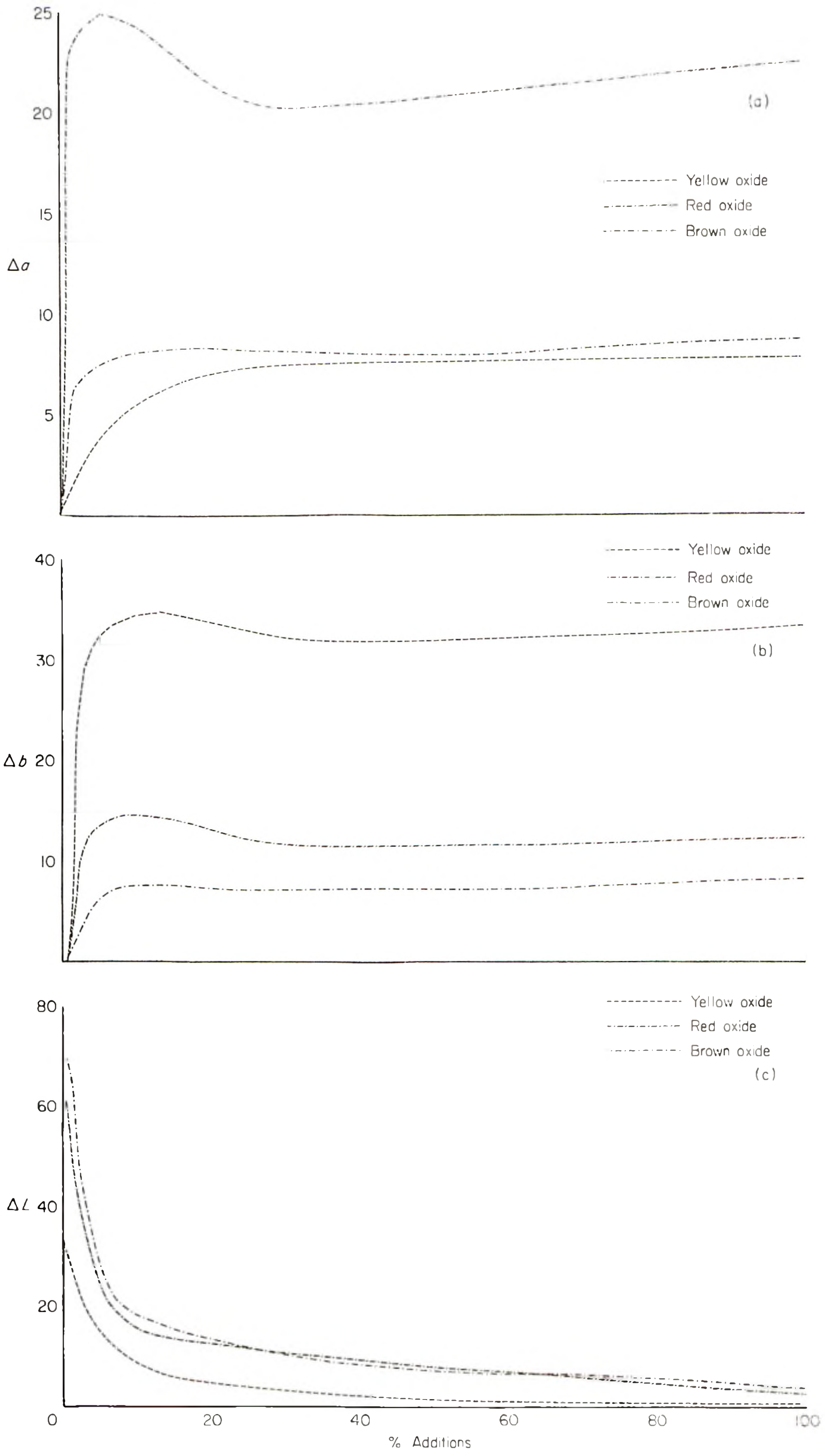


Figure 7. Graph of talc with added oxide pigment against (a) '*a*'; (b) '*b*'; (c) '*L*'.

equally interesting. As the concentration of each pigment increases, '*L*' diminishes indicating that the mixture gets darker—the red and brown oxides have a more marked effect than the yellow. Once again, however, the greatest effect is seen over the 0–5% concentration range. The lesson which we learned from these experiments was that the addition of more than 5% of oxide pigments causes no further colour change and merely darkens the product—an effect which can be achieved more economically by the addition of a neutral black.

Having thus familiarized ourselves with the instrument and the colour space in which it operates, we began to devise a programme of work for it. Our prime objective was to find a means of using the instrument to improve the efficiency of our in-process colour correction as we did with the absorption spectrophotometer, but first it was necessary to discover just how close the sample co-ordinates had to be to the standard co-ordinates before the match became visually acceptable.

THE ESTABLISHMENT OF TOLERANCES FOR COLOUR FUNCTIONAL COSMETICS USING TRISTIMULUS COLOUR MEASUREMENT

Unlike many other colour-orientated businesses, cosmetics manufacturers have only one category of customer—the unknown and unseen with whom it is impossible to establish colour tolerances in advance. Each manufacturer has therefore to establish his own idea of what constitutes an acceptable match to standard and in consequence, he usually errs on the conservative side. Cosmetics manufacturing, however, is not exempt from the common laws of good business practice; a sample rejected when it actually would be acceptable to the customer resulting in expensive re-working can be just as wasteful as a sample accepted when it is actually out of tolerance, resulting in an unhappy customer. However, it only becomes possible to know if both types of mistakes are being minimized if some objective numbers are used for describing the acceptance/rejection boundary—the colour matcher cannot be relied upon unaided.

Table III illustrates the result of an experiment conducted at Yardley in which 56 people were asked to evaluate 14 samples of face powder with respect to their acceptability as a match to the same standard. Twelve of the samples were prepared by making known additions of one of the four coloured components (red, yellow, brown and base) to the standard batch, each sample being 'pressed out' with an aliquot of standard in the manner used routinely at Yardley for batch colour correction. Two standards were

Table III. Face powder pass/fail colour experiment

Operator		Sample No.														
No.	Sex	1	2	3	4	5	6	7	8	9	10	11	12	13	14	Total
1	M	×										×		×		3
2	M	×						×			×	×		×		5
3	M	×						×			×	×		×		5
4	M	×	×				×		×	×		×	×	×		8
5	M	×		×				×		×		×	×	×		7
6	M	×				×		×				×		×	×	6
7	M	×		×	×			×		×		×		×		7
8	M	×		×				×				×		×		5
9	M	×		×		×		×			×	×		×		7
10	M	×						×		×		×		×		5
11	M	×		×				×	×	×	×	×		×		8
12	M	×						×		×		×		×		5
13	M	×						×		×		×		×		5
14	M	×						×				×		×		4
15	M	×				×		×	×	×		×		×	×	8
16	M	×		×	×	×		×				×		×		7
17	M	×	×	×	×			×				×		×		7
18	M	×				×		×					×	×		5
19	M	×			×				×				×	×		5
20	M	×				×		×		×		×	×			6
21	M							×						×		2
22	M	×						×				×		×		4
23	M	×				×		×		×		×		×		6
24	M	×						×				×		×		4
25	M	×		×			×	×		×		×	×	×		8
26	M	×				×		×		×		×		×		6
27	M	×						×				×		×		4
28	M	×						×				×		×		4
29	M	×						×				×	×	×	×	6
30	M	×		×	×		×	×		×		×		×		8
31	M	×						×				×		×		4
32*	M	×	×	×	×	×		×	×	×	×	×	×	×		12
33	F	×						×				×		×		4
34	F	×		×				×				×		×		5
35	F	×				×		×				×		×		5
36	F															0
37	F	×				×		×			×	×		×		6
38	F	×		×		×		×				×		×		6
39	F	×						×		×		×		×		5
40	F	×		×				×				×		×		5
41	F	×	×		×			×		×		×		×		7
42	F	×						×				×		×		4
43	F	×		×				×		×		×		×		6
44	F	×						×				×		×		4

× = Fail.

Table III continued

Operator		Sample No.														
No.	Sex	1	2	3	4	5	6	7	8	9	10	11	12	13	14	Total
45	F													×		1
46*	F	×		×	×	×	×	×	×	×	×	×	×	×	×	13
47	F		×	×	×			×	×			×	×	×		8
48*	F	×		×	×	×	×	×		×	×	×	×	×	×	12
49	F	×		×		×		×	×	×	×	×		×		9
50	F	×			×	×		×		×			×	×		7
51*	F	×		×		×	×	×		×	×	×		×	×	10
52	F	×		×								×		×		4
53	F	×						×				×		×		4
54*	F	×		×	×	×	×	×	×	×	×	×	×	×		12
55	F	×						×			×	×		×		5
56*	F	×	×	×	×	×	×	×	×	×	×	×	×	×		13

× = Fail.

included as an additional test of discriminatory performance. The 56 examiners (who represented a cross-section of laboratory and factory personnel) were asked merely to say whether each sample was a 'satisfactory' match to the standard: in most cases, this was interpreted as 'is there a perceptible difference?' Details of how each sample was obtained from the standard are given in *Table IV.* Six of the examiners—those marked with an asterisk in *Table III*—were professional colour discriminators whose full time job routinely involved colour matching. It will be seen that this group were much more strict than the rest.

Table IV. Composition of samples used in experiment reported in *Table III*

Sample	Composition
1	Standard + 20% Extended yellow
2	Standard + 5% Base
3	Standard + 5% Extended brown
4	Standard + 10% Extended yellow
5	Standard
6	Standard + 10% Extended brown
7	Standard + 10% Base
8	Standard + 5% Extended yellow
9	Standard + 5% Extended red
10	Standard + 20% Extended brown
11	Standard + 10% Extended red
12	Standard + 50% Extended brown
13	Standard + 20% Base
14	Standard

It can be argued that an operator taken from within the professional group would be 2.4 times more likely to fail a sample than an operator randomly selected from the larger group. Which group most closely reflects the opinion of our customers? How much faith can be put in the professionals' power of discrimination when all six would have failed one of the standards and three of them *both* standards? Does this mean that the company is wasting money by re-working acceptable batches of powder? These are interesting questions with no clear-cut answers, but one thing which seems to emerge from this and similar experiments is that human colour matchers are every bit as human as the rest of us. They have doubts, they have off-days and they do their job as conscientiously as possible. Tristimulus colour measurements can help by putting an objectively determined number (or numbers) on a subjectively evaluated quality, thus allowing the subjective quality to be treated in the same manner as some physical characteristic such as length or weight.

Fig. 8(a)–8(c) illustrate the use of colour difference graphs in which differences between the co-ordinates relating to the standard and sample are plotted against each other. In *Fig. 8(a)*, for example, the difference between 'a' values, Δa (sample minus standard) are plotted against the difference between 'b' values, Δb (sample minus standard) for a number of accepted batches of a light-coloured face powder. The actual co-ordinates of the standard material were $L=74.0$, $a=+8.4$, $b=+12.7$ but its position on the $\Delta a/\Delta b$ diagram is at point 0,0 in the very centre of the graph. Any marked position above the $\Delta b=0$ line represents a batch which was accepted more yellow (or less blue) than standard and any below the line was passed less yellow (or more blue) than standard. Similarly, any point to the right of the $\Delta a=0$ line marks the position of a batch accepted more red, or less green, than standard and any to the left of the line were less red or more green than the standard. The further from the centre the position of a sample, the further away from the standard colour it is. It would be convenient if a circular 'acceptance zone' of fixed radius could be drawn around the centre so that any sample with co-ordinates falling within the circle could be passed. Unfortunately, however, the data illustrated in *Fig. 8(a)* do not justify it since there is only one point situated in the upper left quadrant.

Fig. 8(b) and *8(c)* (showing $\Delta L/\Delta a$, $\Delta L/\Delta b$ respectively) provide even less justification for such a symmetrical simplification. It is evident that the spread of points along the ΔL axis is much greater than along the other two. It is tempting to speculate that because L, a, b, colour space is not perfect and the three-colour scales are only approximately equivalent in

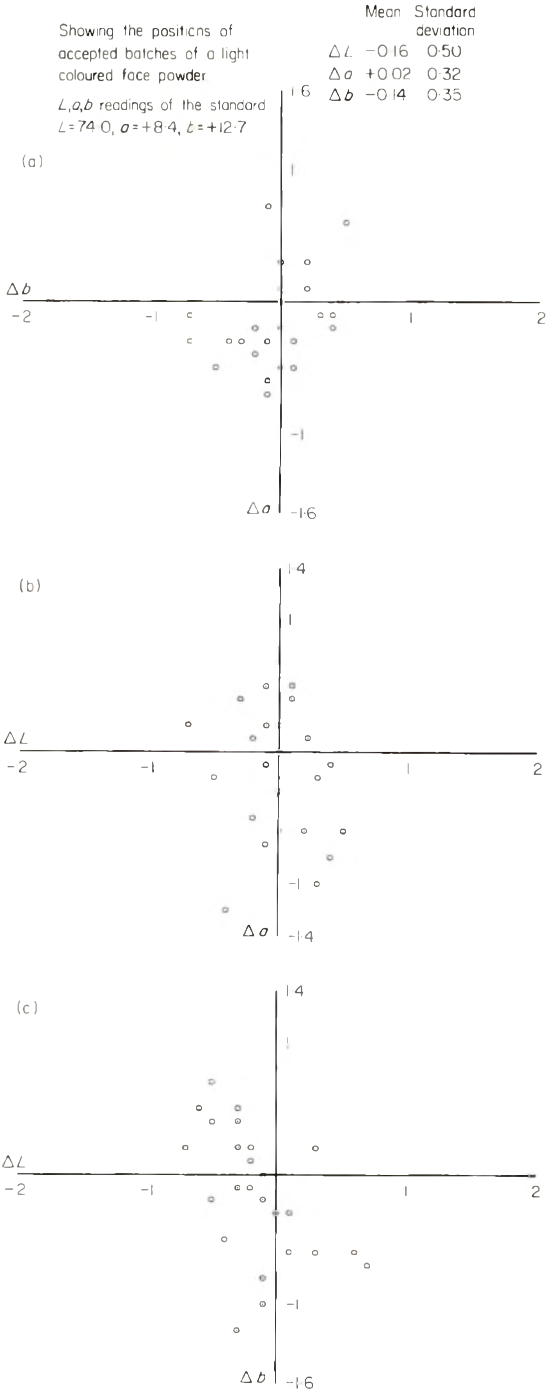


Figure 8. Colour difference graph (a) ($\Delta a/\Delta b$); (b) ($\Delta L/\Delta a$); (c) ($\Delta L/\Delta b$).

expressing degrees of difference that the theoretical circle of acceptance has been transformed into an ellipse by the use of non-equivalent radii. This may be partially true, especially for graphs involving ΔL since the square root function is only very approximate. In any event, the precise shape of the area of acceptance will have to wait until many more points have been plotted.

Fig. 9(a)–9(c) show similar data obtained from a very dark shade of powder. Although the general pattern is similar to that obtained from the light shade, it is interesting to note that the vast majority of accepted batches were yellow to standard. Subsequent experiments verified that, for this shade, small positive differences in '*b*' were hardly noticeable, whereas negative differences were not generally acceptable.

Such graphs are being compiled for a variety of shades and products in our laboratory. In many cases, the pattern which is beginning to emerge seems to be approximately ellipsoid in shape. *Fig. 10* represents a $\Delta a/\Delta b$ graph showing the tentative area of acceptance for the same shade of face powder to which the spectrophotometric curves of *Fig. 5* relate. The *L*, *a*, *b* co-ordinates for this particular standard show it to be of intermediate lightness to the shades illustrated in *Figs. 8* and *9*. *Fig. 10* also shows the path taken by this troublesome batch during the correction procedure described in *Table II*.

It seemed to us that the precise shape of the area of acceptance was of little consequence so long as it could be determined for each individual shade of the product. Evidently, however, if such determinations depend upon the plotting of numerous sets of co-ordinates from acceptably matched samples, then the process can only be useful in extremely long-lived product lines. We continue to plot such data, however, even for short-lived fashion items for the following reasons:

We feel as others have done (2), that with experience we may be able to deduce some means of correctly anticipating the acceptance zone for a given area of colour space.

By dating each point plotted, indications of trends and variations between individual matchers are obtained.

The graphs provide a further piece of evidence to help the matcher make up his mind in difficult circumstances.

By combining such graphs with experiments of the sort illustrated in *Table III*, we hope to be able to tell whether we are wasting money by being too cautious in our assessment of an acceptable match.

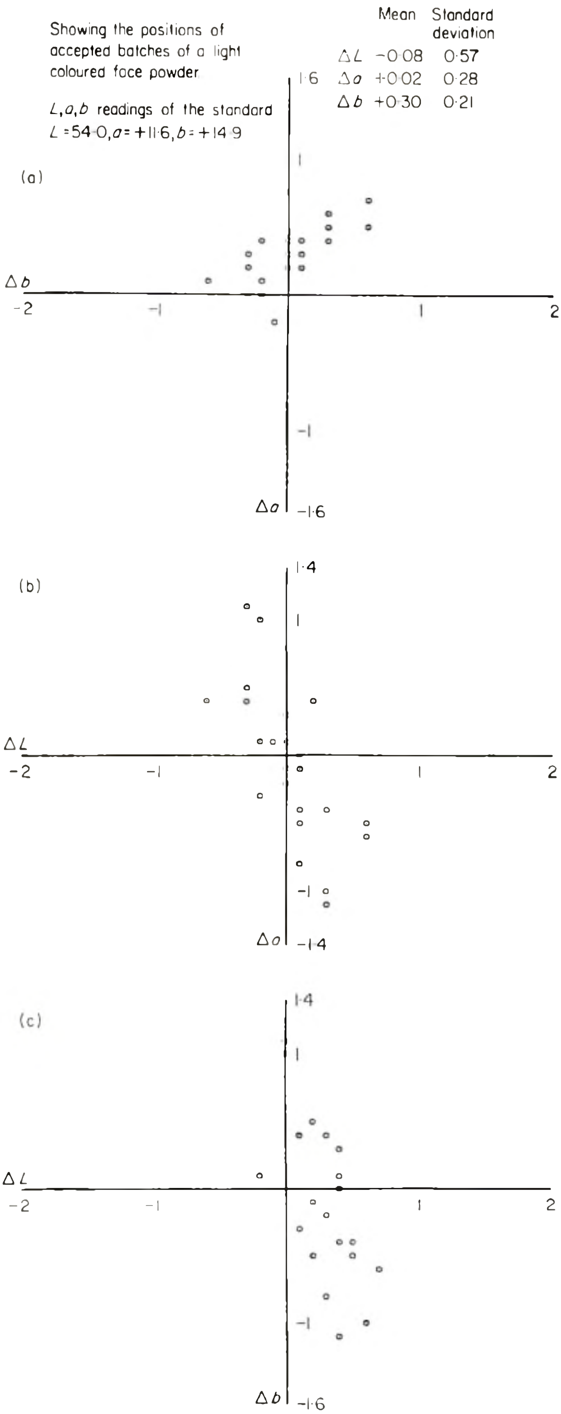


Figure 9. Colour difference graph (Δ*a*/Δ*b*); (b) (Δ*L*/Δ*a*); (c) (Δ*L*/Δ*b*).

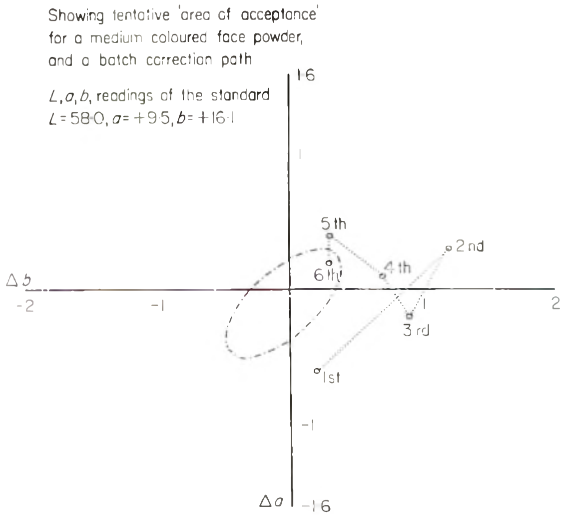


Figure 10. Colour difference graph ($\Delta a/\Delta b$).

TRISTIMULUS COLOUR MEASUREMENT AS AN AID IN THE COLOUR MATCHING PROCESS

It could easily be imagined that if the Hunterlab had been available to the operator responsible for the correction procedure detailed in *Table II*, and he (or she) had plotted it as it proceeded, as in *Fig. 10*, then the match would have been arrived at much sooner. We decided to go one step further than this by determining whether the effect on L, a, b, of adding known concentrations of the various coloured components could be calculated in advance, so as to achieve an acceptable match in a single correction.

Fig. 11(a)–11(d) show graphically the effects (in terms of ΔL, Δa, Δb) of adding increasing concentrations of the four colour components (red, yellow, brown and base) of a face powder to the standard material. The graphs themselves require little comment except that the brown and base appear predominantly to control the 'L' value with little effect on 'a' and 'b': this is in keeping with the subjective assessment of colour matchers for products of this type. It is also worth noting that the linear relationship breaks down to some extent as the origin is closely approached. The explanation for this is not yet clear. The validity of these data and their mode of use is illustrated by the following actual examples.

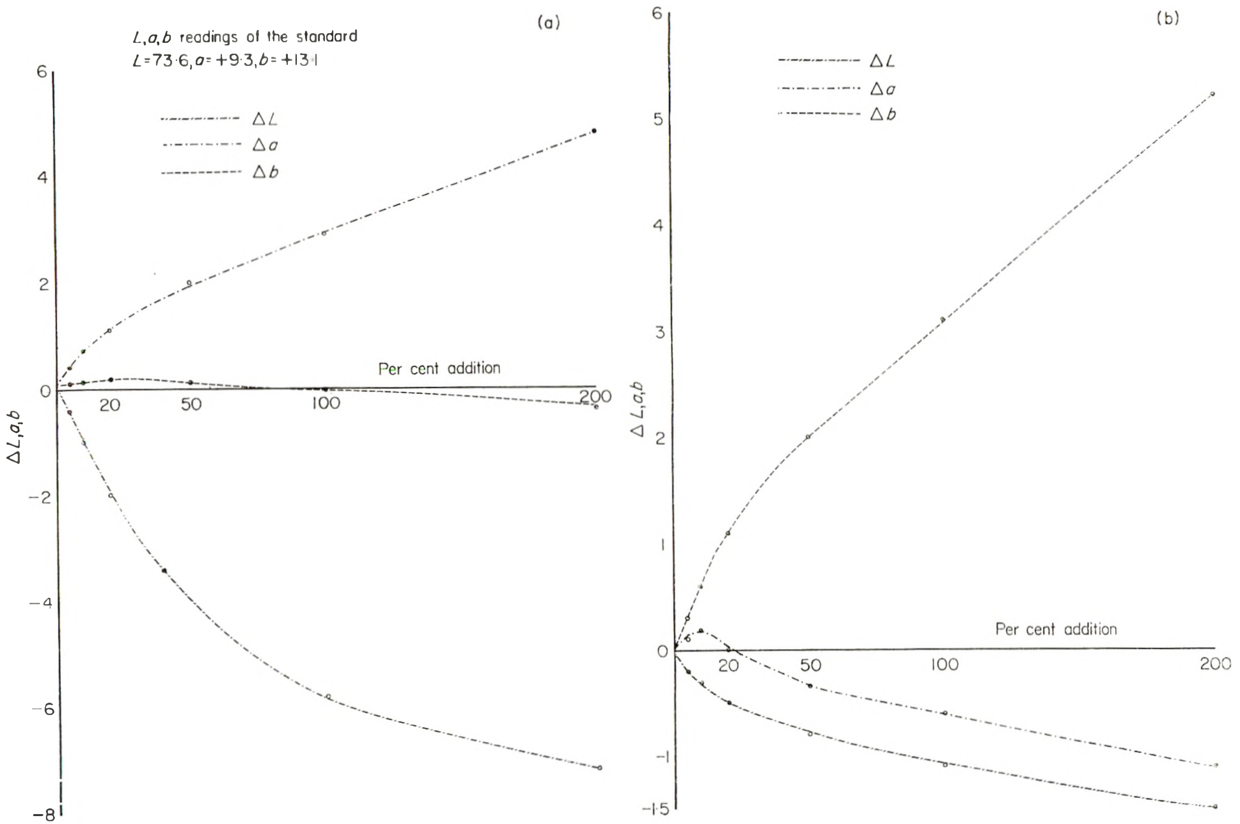


Figure 11. Changes in L, a, b with extended (a) red*, (b) yellow*, (c) brown* and (d) base additions to a standard face powder.

* 20% extensions in talc

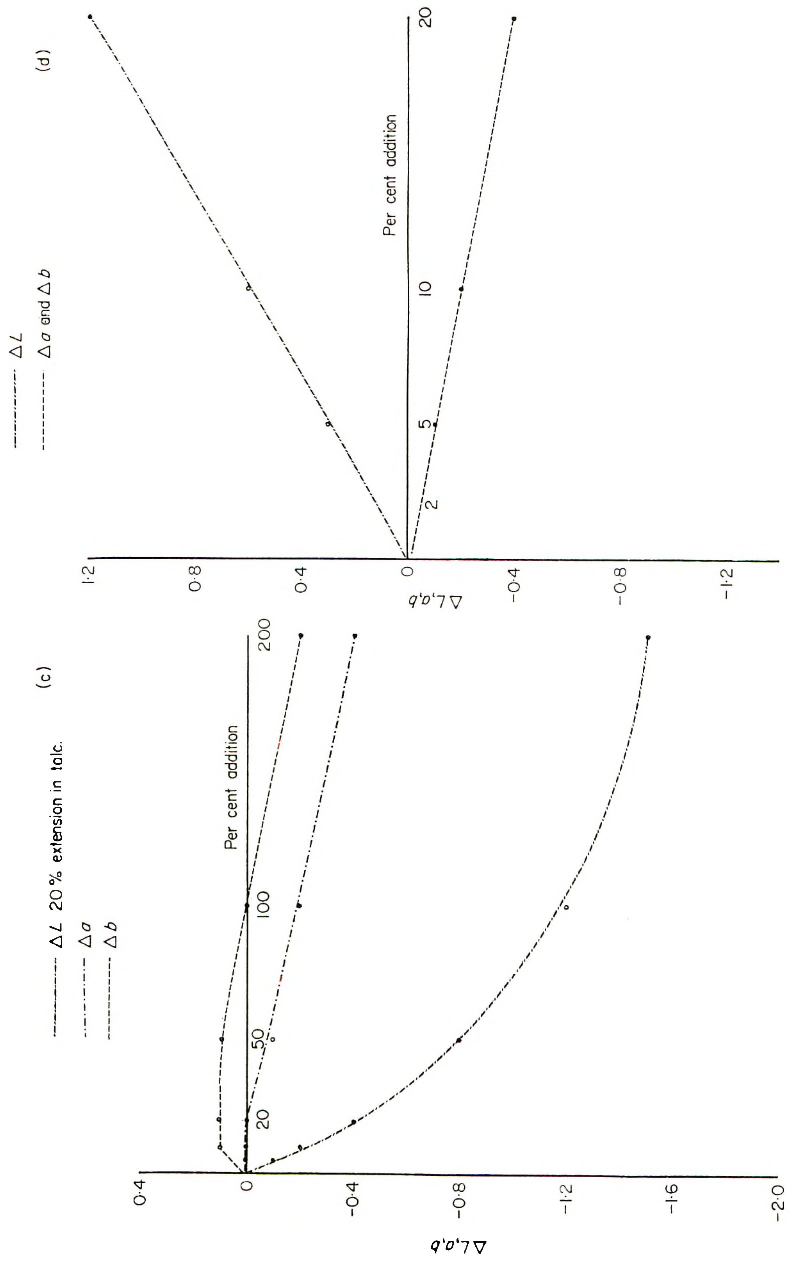


Figure 11. c and d.

Example 3—Tristimulus match, 4 colours

Product	Face powder		
Composition	Base + red, yellow, brown oxides		
L, *a*, *b* values:			
sample	$L=74.8$	$a=+9.2$	$b=+12.8$
standard	$L=73.6$	$a=+9.3$	$b=+13.1$
Problem	What quantities of extended oxides must be added to achieve a match to standard?		

The required changes are: $\Delta L=-1.2$, $\Delta a=+0.1$, $\Delta b=+0.3$.

From *Fig. 11(b)* the required increase in '*b*' can be obtained from a 5% addition of yellow. This will have little effect on '*a*', but will decrease '*L*' by 0.2. The further decrease of 1.0 required for '*L*' is shown in *Fig. 11(c)* to be achieved by the addition of 85% brown with little change in '*a*' or '*b*'.

Calculated correction: +5.0% yellow, +85% brown.

Result: Sample now reads $L=73.2$, $a=+9.3$, $b=+13.2$.

Visual assessment: A good match.

Example 4—Tristimulus match, 4 colours

(Product, composition and standard as in Example 3)

L, *a*, *b* values			
Sample	$L=72.9$	$a=+9.4$	$b=+14.2$
Problem	What quantities of extended oxides must be added to achieve a match to standard?		

The required changes are: $\Delta L=+0.7$, $\Delta a=+0.1$, $\Delta b=-1.1$.

Here, the required correction for '*b*' is larger than we have data to deal with. It will require a shot onto the green before we can sink a putt.

1st Correction: +40% base.

(This, extrapolating the data from *Fig. 11(d)*, should bring us onto the graph.)

Result: Sample now reads $L=75.6$, $a=+8.1$, $b=+12.8$.

From *Fig. 11(a)* the change in '*a*' can be obtained from a 25% addition of red, which will alter *L* by − 2.2.

2nd Correction: +25% red.

Result: Sample now reads $L=74.7$, $a=+9.5$, $b=+12.9$.

The new *L* value is unexpected, but from *Fig. 11(c)* both the required changes in '*L*' (− 1.1) and '*a*' (− 0.2) should arise from the addition of 150% brown.

Correction: +150% brown.
Result: Sample now reads $L=73.2$, $a=+9.3$, $b=+12.9$.
Visual assessment: A good match, but sample showing slight geometrical metamerism.

In this case the correction was less easy since the sample started out much too dark (too much brown and yellow had been added to it). Nevertheless, a reasonable match was achieved with three corrections; for a sample so far from the standard, this would have been no mean feat for the unaided colour matcher.

For less complicated cosmetics, *Fig. 11(a)–11(d)* can be replaced by 'skew axis' graphs of the sort illustrated in *Fig. 12*. This relates to a pearly powder eyeshadow product composed of two blue pigments and a base.

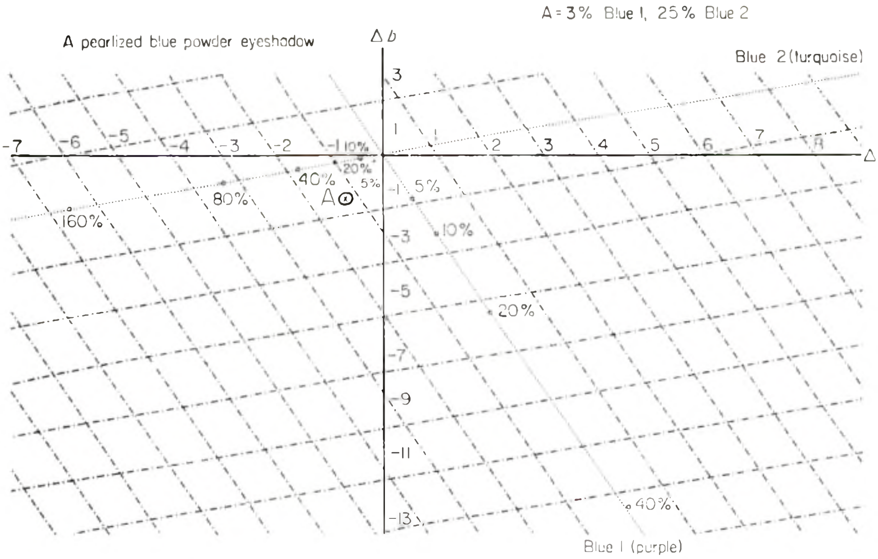


Figure 12. 'Skew' axis colour difference graph ($\Delta a/\Delta b$).

Such a graph is prepared by plotting the differences in each dimension from the standard resulting from the addition of known quantities of each pigment to the standard batch. The 'skew' axes are then drawn through each line of points and a grid of parallel lines constructed. A batch sample having differential co-ordinates situated at A, for example, would require approximately 3% of blue 1 and 25% of blue 2 to get to the same 'a' and 'b' co-ordinates as the standard.

FURTHER EXAMPLES OF THE APPLICATION OF COLOUR MEASUREMENTS IN A COSMETICS LABORATORY

We have found that tristimulus colour measurements are applicable to problems other than colour matching within our laboratory, especially those concerned with the storage testing of raw materials and products. *Table V*, for example, relates to three alternative blue foam bath formulae.

Table V. Appearance changes produced during 24 h fade test on three bath foams with varying quantities of UV absorber

Foam Bath	1			2			3		
Change	ΔL	Δa	Δb	ΔL	Δa	Δb	ΔL	Δa	Δb
No UV absorber	+4.9	+15.3	+5.9	−1.4	+10.6	+0.6	−4.0	+16.8	−1.6
0.1% UV absorber	+3.9	+10.5	+4.6	−0.3	+6.7	+0.9	−2.4	+11.1	−0.2
0.2% UV absorber	+4.9	+10.7	+4.7	+1.6	+4.0	+1.4	−2.9	+8.9	−0.9

Since actual numbers can be meaningfully applied to these appearance changes, it becomes much easier to rate the relative performance of each formulation in the fade test. In addition, these data also indicate an unexpected relationship between the amount of UV-absorber added and the subsequent change in appearance of the product—a clue worth following up.

Table VI relates to the storage testing of a certain shade of soap made from alternative soap bases. Once again, the value of these data lies in the acquisition of meaningful figures concerning subjective appearance differences by which means the relative performance of each base can be assessed in relation, for example, to its cost.

Table VI. Changes in the appearance of finished soap made from two soap bases during laboratory storage test procedures of 1 month duration

Base	1			2		
Change	ΔL	Δa	Δb	ΔL	Δa	Δb
4°C	−4.1	+3.8	−4.2	−0.8	−10.7	−0.4
Ambient	−4.8	+4.4	−5.0	−1.2	+1.2	−0.5
Cycle*	−3.4	+4.1	−2.9	−0.8	+1.3	+0.1
32°C	−4.7	+4.4	−4.3	−0.8	+1.2	0.0
37°C	−3.6	+4.0	−3.6	−1.5	+1.3	−0.3
46°C	−3.6	+3.8	−1.8	0.0	+1.4	+1.0

* 4°C–46°C twice in 24 h.

Finally, an interesting problem arose in our laboratory because of our policy of shipping unperfumed face powder to some of our overseas companies for subsequent perfuming by them before sale. It was noted that the addition of the perfume in each case caused a significant appearance change.

Table VII. Appearance changes produced by the addition of perfume to un-perfumed face powders

Face powder shade no.	ΔL	Δa	Δb
1	+0.6	+0.2	+0.2
2	−2.5	+0.4	0.0
3	−0.5	+0.2	−0.2
4	−0.7	0.0	+0.4
5	−1.1	+0.2	+0.4
6	−3.4	+1.1	+0.5

These were monitored as indicated in *Table VII* and from these data, new standards were devised for the unperfumed powders, so that the final products would be on shade.

DISCUSSION AND CONCLUSIONS

This report has ranged over a number of instrumental colour-assessing techniques and over a number of product types. We have found, in each case, that instrumental differences have always been obtained from samples showing perceptible visual differences. Certain of the techniques have yielded sufficiently useful information to justify incorporating them into our routine colour assessment and colour matching procedures and we have been happy with the results of so doing. The difficulties of such an undertaking, however, should not be underestimated: some of the calibration procedures are lengthy and require care. Some products are less susceptible to instrumental techniques than others—particularly highly pearlized lipsticks and eye make-up products. Nevertheless, we do not consider that any of these problems are insurmountable.

Of the three categories of promise listed at the beginning of this paper, we feel justified in concluding that some of the techniques examined have fulfilled at least the first two. As for the third, we are not yet anxious to have attractive female colour matchers replaced by a mere instrument, no matter how efficient it may be!

ACKNOWLEDGMENTS

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A method to evaluate the tube-squeezing properties of toothpaste

BENGT NORÉN*

Synopsis—A method has been evolved to evaluate the tube-squeezing properties of TOOTHPASTE using a simple inexpensive squeeze device. A toothpaste tube on squeezing shows the rheological properties of a PSEUDO-PLASTIC material. A squeeze equation has been derived and used to estimate the output from a tube under different squeeze conditions to give good correlation with empirical results.

Both toothpaste and tube contribute to the squeeze behaviour of the product and consequently both must be taken into consideration when the product is evaluated.

Examples are given of the changes of squeeze property with storage and the effect of variable gain content and tube dimensions.

INTRODUCTION

The tube has been used as packaging material for more than a century. The first tube patent was registered in London as early as 1841 by John Rand. At this time the tubes were made of lead or tin and it was not until just before the Second World War that aluminium tubes appeared on the market. New tube materials are still being developed and today's various plastic tubes are being superseded by plastic–aluminium laminated tubes.

Many household products besides toothpaste are packed in tubes. Any tube product must have a suitable viscosity, neither too stiff to make it

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difficult to get it out of the tube, nor so soft that it runs out when the tube is opened.

Besides the viscosity of the tubed product, the tube material and tube and orifice diameters may have an influence on extrudability.

Many methods are used to measure the viscosity of the tube contents from simple penetrometry to more advanced rheological measurements with structure viscometers. Although these give an indication of the flow behaviour of the content of the tube it only gives a hint of the product's squeeze properties when used by a consumer.

A better way to characterize this is to measure the extrusion force necessary to extrude the product through some kind of orifice. This has been done for extrusion of pastes and creams and other semi-solids from tubes and bottles (1–3). Block (4) described an extrusion method used to evaluate toothpaste. By using an Instron tensiometer he measured the extrusion force by extruding the toothpaste from its original tube. He also found that the ease of extrusion was related to the initial force of extrusion. Wood *et al.* (5) described a method that more accurately simulated the way the consumer squeezes a plastic bottle or tube. They made a small test device using a 'thumb' to press tubes and plastic bottles.

The methods mentioned here are rapid and thus suitable for product control where relative figures are sufficient. However, they do not permit any calculation of the output from the tube or bottle when squeezed with a known force and during a known period of time, simply because they do not take into consideration all forces involved in the squeeze process, eg the force required to deform the packaging or to redistribute the product within the container when not entirely filled. One exception is the method described by Wood and coworkers.

The intention of this work was to develop a method, which would simulate tube-squeezing as it is performed by a consumer and to have the possibility of calculating the output from the tube under different conditions. An attempt was made to find a relationship between squeeze properties and viscosity.

EQUIPMENT

The device is seen in *Figs 1 and 2* and works as follow. The tube (t) is placed between two 'fingers' opposite each other, one fixed finger (ff) and the other moving (mf). The moving finger is mounted on the axis of a pneumatic dashpot (d) (Mecman, series 1300, piston diameter 20 mm). By letting

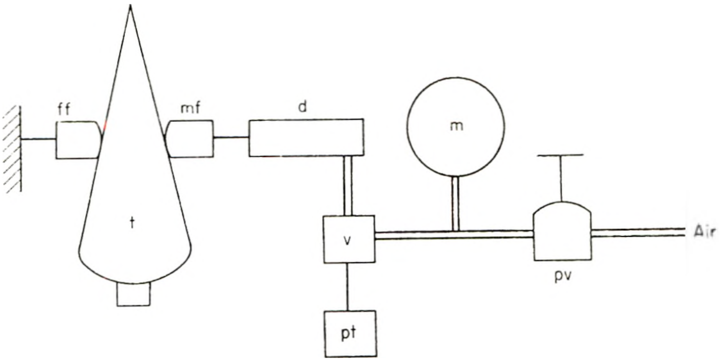


Figure 1. Schematic drawing of the squeeze-test device.

pressurized air into the dashpot the moving finger is pressed towards the fixed one and the tube is squeezed. The air pressure is controlled by a precision valve (pv) (Mecman 11–918–110) and checked by a manometer (m) (gauge 0–10 kp cm^{-2}.) Between the precision valve and the dashpot there is an on–off valve (v) (Mecman, 412/310, 220 V/50 Hz) controlled by a phototimer (pt) (T. Baeuerle & Sohne, St Georgen im Schwartzwald, Germany), by which the squeeze time is set. Finally the device is connected to a pressurized air supply (air). Thus the parameters—squeeze time and squeeze force—can be set by the investigator. The fingers—made of PVC—are cylindrical with a diameter of 20 mm. The edges of the surfaces facing the tube are slightly rounded in order not to cut through the tube wall. The tube is placed so that the fingers will squeeze it in its *middle*. This squeeze device enabled us to reproduce the conditions of tube squeezing.

The squeeze force is calculated from the air pressure by the equation.

$$P = A \cdot \varphi \cdot 9.81 - \Delta P \qquad (1)$$

where P = squeeze force (N),
A = piston area (= π cm^2),
φ = air pressure (kp cm^{-2}),
ΔP = friction forces (N).

The friction forces are considered small and are thus neglected.

EXPERIMENTAL

The squeeze process was studied by varying the squeeze time and the squeeze force and measuring the output from the tube. The output was determined by weight to 10 mg accuracy. It was found that there were individual differences in the outputs between tubes, which made it necessary to calculate the output as a mean from a number of tubes. Four to six tubes were used to get the mean value.

A general picture of the output (ΔG) from a toothpaste tube and the corresponding standard deviations at 15 consecutive squeezes is shown in *Fig. 3*. It is seen that the output is dependent on how full the tube is. This is due to the fact that when squeezing a filled tube the contents have nowhere to go but out through the orifice. When the tube is less full there is a possibility for the content to be redistributed within the tube before it extrudes through the orifice. Consequently the output decreases. This is easily observed in practice with filled and half-filled tubes. It is far easier to get the desired amount out of the full tube than it is to get it out of the half-filled one. In addition to the degree of filling or squeeze number both squeeze time and squeeze force affect the output. When taking those three factors into consideration a general squeeze equation can be written.

$$\Delta G = f(n,t,P) \tag{2}$$

where ΔG = output from tube (g),
n = squeeze number,
t = squeeze time (s),
P = squeeze force (N).

The general appearance of the squeeze curve obtained from different tubes and constant squeeze time is shown in *Fig. 4*. The resemblance to the flow curve of a pseudo-plastic material is apparent where the output corresponds to shear rate and the squeeze force corresponds to shear stress (*Fig. 5*.) The squeeze curve for the system tube-toothpaste also has an established yield value (P_0) above which the output is proportional to the squeeze force.

The squeeze curve in *Fig. 4* can be divided into the following three parts:

At low squeeze forces, below the yield value, the output is small and of no importance. Squeeze forces of this magnitude will hardly give the desired output.

When the squeeze force exceeds the yield value the output is proportional to the applied force up to a limit (P_{max}), where the tube starts emptying.

At squeeze forces exceeding P_{max} the output can no longer be increased as the maximum accumulated output is reached. This effect appears at still lower forces for subsequent squeezes.

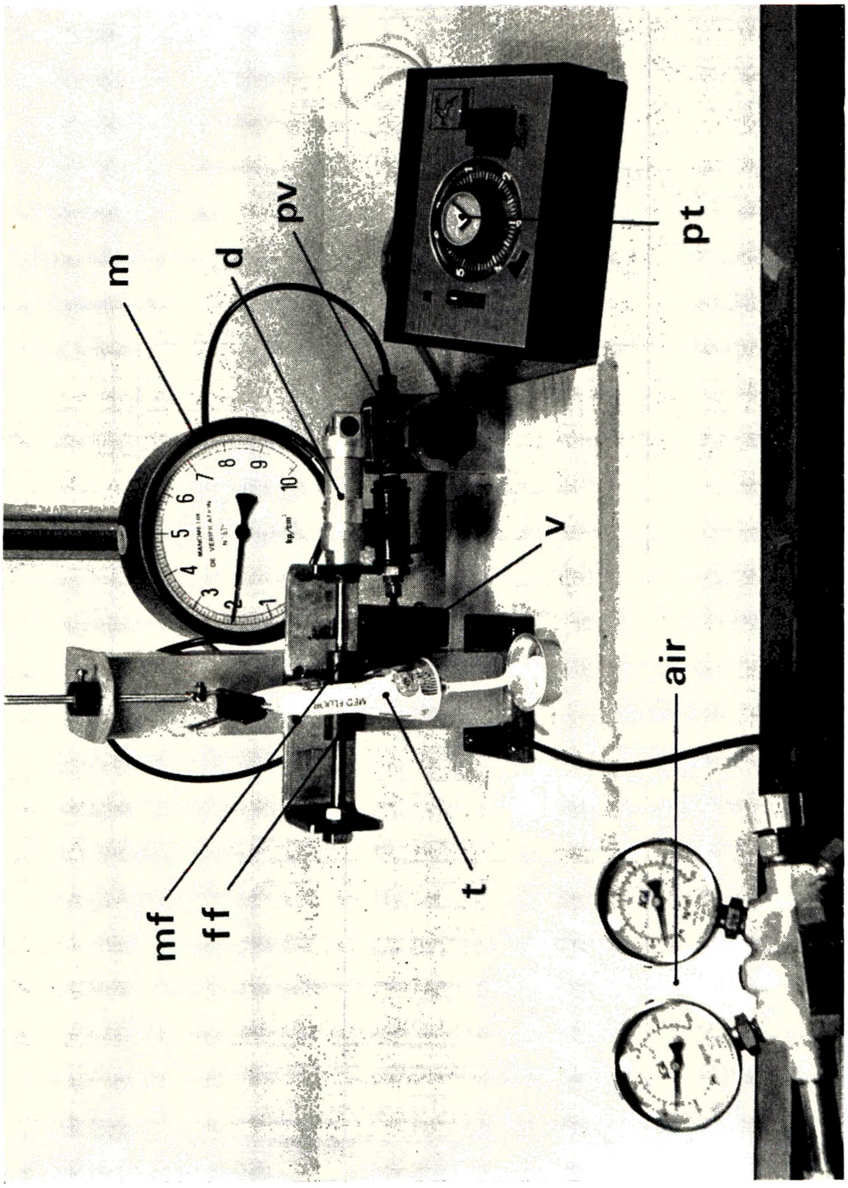


Figure 2. The squeeze-test device.

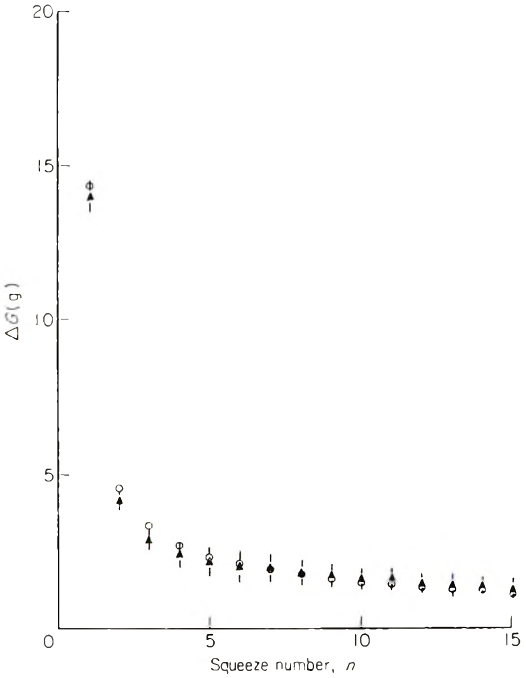
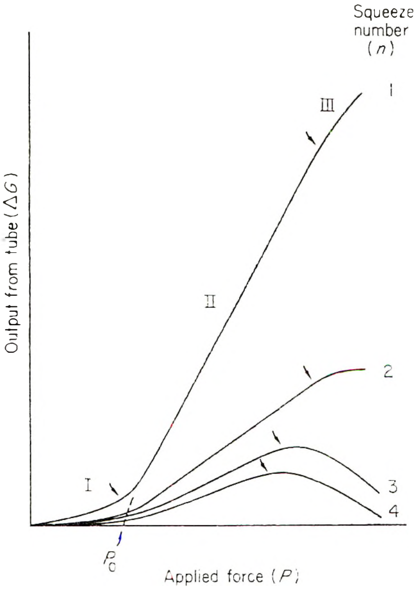


Figure 3. Toothpaste output, ΔG (g) froma 160 g-tube at 15 consecutive squeezes. Squeeze force 62 *n*. Squeeze time 0.5 s. ▲, found value. ○, calculated values from equation (12).



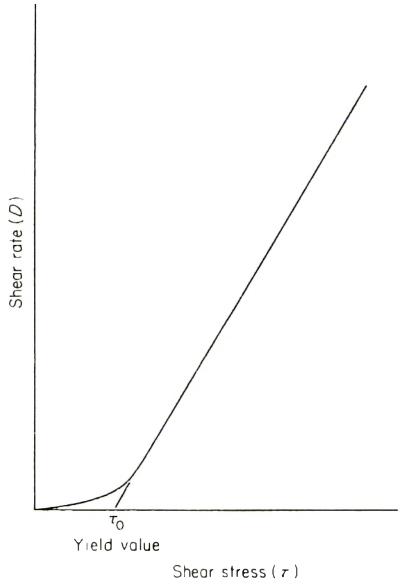


Figure 4. General appearance of the squeeze curve. Output from tube as a function of squeeze force. Squeeze time constant.

Figure 5. Flow curve for a pseudo-plastic material.

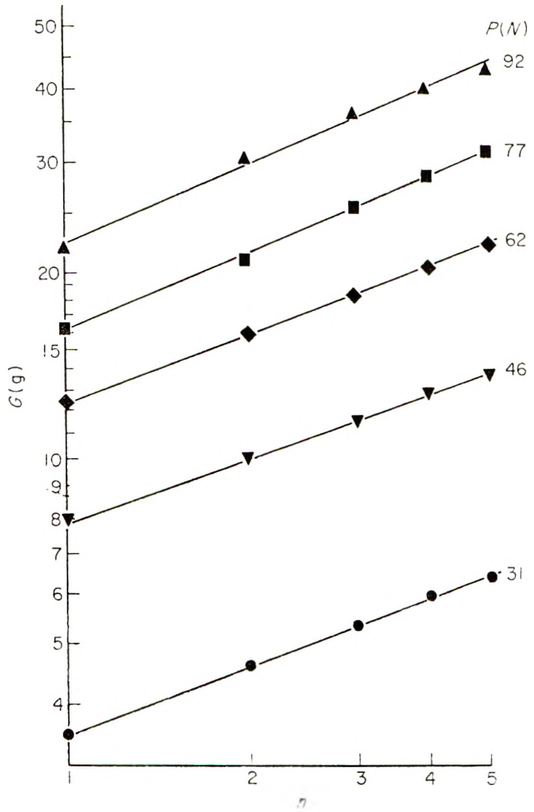


Figure 6. The accumulated output *vs* squeeze number. Squeeze time 0·5 s.

The yield value was found constant and independent of squeeze time and squeeze number.

The linear part of the squeeze curve was observed by Wood and co-workers (5). It has now been further investigated by us as it is considered the most important part of the curve and a squeeze equation was established for it. In the following the evaluation of this part of the curve is exemplified by figures obtained from a typical toothpaste.

A linear relationship is found between the logarithmic accumulated output (log G_n) and the logarithmic squeeze number (log n) (*Fig. 6.*) The curve is linear up to that point where the tube cannot further be squeezed. Thus

$$\log G_n = \beta \cdot \log n + \log G_1 \tag{3}$$

$$\text{or } G_n = G_1 \cdot n^{\beta}. \tag{4}$$

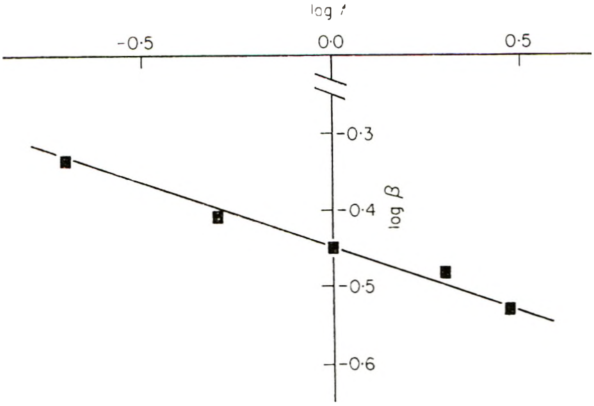


Figure 7. The squeeze time dependence of exponent β from equation (7).

The accumulated output is defined as the sum of all individual outputs

$$G_n = \sum_{i=1}^{n} \Delta G_i \tag{5}$$

From equation (4) the output for squeeze number n is calculated.

$$\Delta G_n = G_1\{\cdot n^{\beta} - (n-1)^{\beta}\}. \tag{6}$$

The exponent β is dependent of the squeeze time but independent of the squeeze force. Consequently the curves in *Fig. 6* are parallel. The squeeze time dependence on exponent β is logarithmically linear. See *Fig. 7*. This gives

$$\log \beta = b \cdot \log t + \log c \tag{7}$$

$$\text{or } \beta = c \cdot t^{b}. \tag{8}$$

By plotting the initial output obtained from equation (3) *vs* the squeeze force for the different squeeze times the second part of the squeeze curve is obtained (*Fig. 8*). Extrapolation to the P-axis gives the yield value. Values below P_0 are neglected as not belonging to this part of the curve. Thus we get for $P_0 < P < P_{max}$.

$$G_{1,t} = k_t \cdot (P - P_0) \tag{9}$$

where k_t is the slope of the curve.

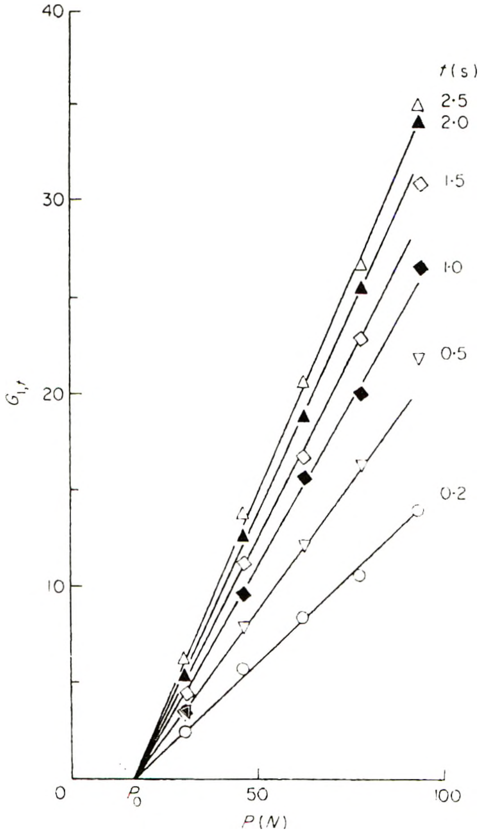


Figure 8. The initial output, $G_{1,t}$, as a function of squeeze force.

The squeeze time dependence of the slope k_t is found to be logarithmically linear. See *Fig. 9*.

$$\log k_t = B \cdot \log t + \log A \tag{10}$$

$$\text{or } k_t = A \cdot t^B \tag{11}$$

Finally by combining equations (6), (9) and (11) we get the squeeze equation.

$$\Delta G = A \cdot t^B \cdot \{n^\beta - (n-1)^\beta\} \cdot (P - P_0) \tag{12}$$

The exponent β is obtained from equation (8).

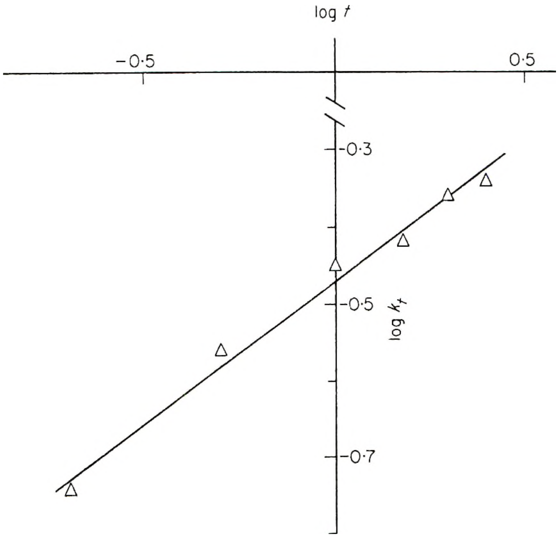


Figure 9. The squeeze time dependence of slope k^t from equation (10).

Once the coefficients A, B, b and c and the yield value P_0 have been determined the output can be estimated in good accordance with empirical values using equations (8) and (12). *Fig. 3* shows both calculated and empirical values. It can be seen that with two exceptions the values are identical.

RESULTS

The squeeze coefficients and yield value for one toothpaste determined on two different occasions with different squeeze conditions are shown in *Table I.* The reproducibility of the method is fairly good.

Table I. Squeeze coefficients and yield value from one toothpaste

Toothpaste	Tube size	A	B	b	c	$P_0(N)$
A 1st	160 g	0.42	0.34	−0.12	0.37	18.7±2.3
A 2nd	160 g	0.43	0.33	−0.13	0.39	19.3±2.7

The squeeze equation also allows us to make more thorough studies on how storage, changes in product composition and how tube dimensions will affect the product's squeeze properties.

Storage

The time from manufacturing a product till it reaches the consumer and is used is generally several months. It is therefore of interest for the manufacturer to know what happens to his product during its shelf-life. Toothpaste is thixotropic and during storage its structure builds up, the viscosity increases, and consequently the extrudability decreases. An example of how storage of toothpaste will affect the squeeze coefficients and yield value is given in *Table II*. Smaller changes are obtained in all constants. However, in practice it is only the changes in A and P_0 that affect the outputs, in this case after 21 weeks storage this means a reduced output of about 33% compared to the one week figure. The increased yield value obtained after 21 weeks does not significantly differ from the one week yield value.

Table II. Changes in squeeze coefficients and yield value during storage of a typical toothpaste. Tube size 160 g

	A	B	b	c	$P_0(N)$
1 week old	0.31	0.35	−0.12	0.41	25.7±4.8
21 weeks old	0.21	0.32	−0.10	0.39	26.3±2.6

Composition

In *Table III* one example is given on how the CMC content of a toothpaste changes its squeeze behaviour. To give the toothpaste time to stabilize its structure the coefficients and yield value were determined 3 months after manufacturing. It is known from experience that an increased CMC content will harden the toothpaste and make it more difficult to extrude from the tube. As seen from *Table III* this is mainly due to two factors. Firstly, the

Table III. CMC content of a toothpaste and its effect on the squeeze coefficients and yield value

% CMC	A	B	b	c	$P_0(N)$
1.13	0.41	0.50	−0.10	0.32	16.0±1.7
1.21	0.42	0.54	−0.09	0.31	16.4±1.1
1.29	0.37	0.58	−0.08	0.34	19.1±2.8
1.46	0.25	0.53	−0.03	0.36	18.6±1.2
1.54	0.17	0.17	−0.06	0.37	22.9±1.7

yield value increases, consequently an increased force is required to exceed the limit where the toothpaste starts to flow out of the tube. Secondly, A decreased significantly, which gives a corresponding decrease of the slope of the squeeze equation, resulting in a decreased output from the tube when squeezed.

Tube dimensions

Commercially available tubes of different sizes were filled with toothpaste from one batch and stored for 2 months prior to the squeeze tests. All tubes had the same length 120 mm but had different tube and orifice diameters. According to the tube manufacturer there was no difference in tube material from one tube size to the other.

The effect of various tube diameters (D) on the squeeze coefficients and yield value is seen in *Figs. 10 and 11.* By increasing diameter B and c increase while A and b decrease up to a tube diameter of 28 mm and then remain constant. The yield value passed a minimum at D = 28 mm. We have no explanation for the obtained minimum, which we find rather unexpected.

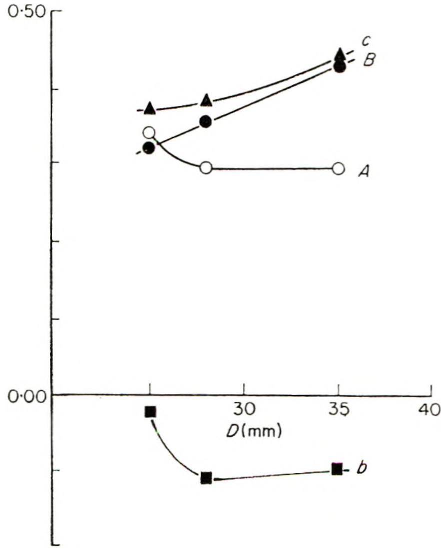


Figure 10. Squeeze coefficients (A, B, b, c) dependence on tube diameter (D). Orifice diameter 6.5 mm. Tube length 120 mm.

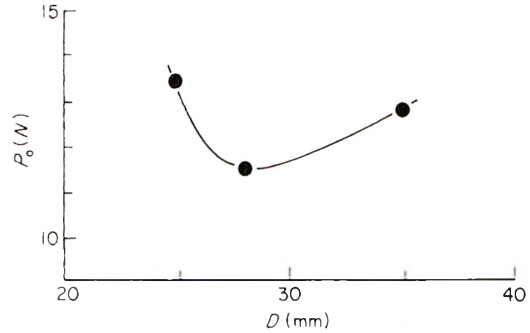


Figure 11. Yield value (P_0) dependence on tube diameter (D). Orifice diameter 6.5 mm. Tube length 120 mm.

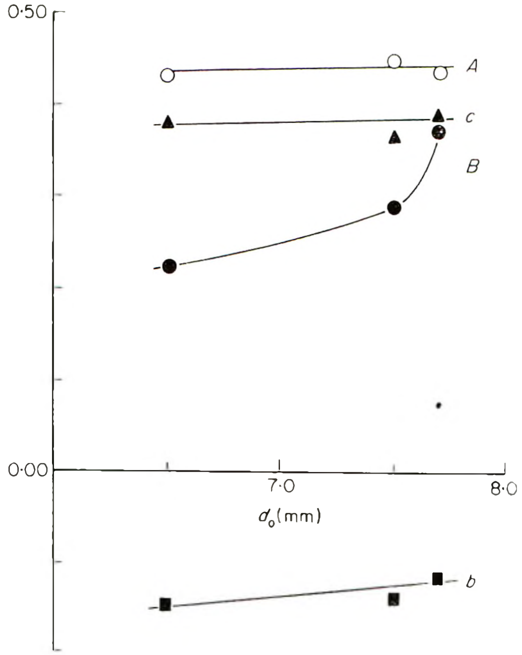


Figure 12. Squeeze coefficients (A, B, b, c) dependence on orifice diameter (d_0). Tube diameter 40 mm. Tube length 120 mm.

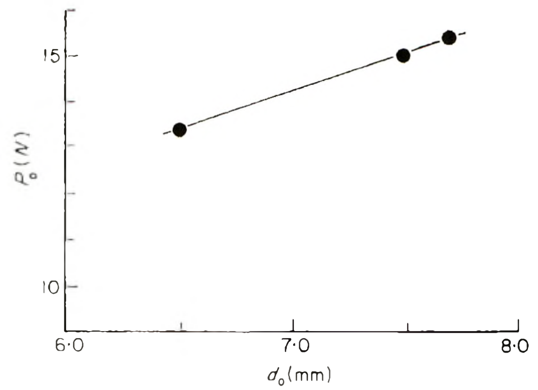


Figure 13. Yield value (P_0) dependence on diameter (d_0). Tube diameter 40 mm. Tube length 120 mm.

An increase in orifice diameter (d_0) does not considerably affect either A, b or c, but will slightly increase B and P_0. See *Figs 12* and *13*. Since these results are from a small number of tube sizes extrapolations outside the plots is not advisable and the conclusions are strictly limited to the studied tube sizes.

Viscosity

We have been unable to find any relation between the squeeze coefficients and the yield value obtained from the squeeze tests and the viscosity and yield value for the toothpaste itself obtained from rheological measurements on a rotating structure viscosimeter (Rheomat 30, Contraves, Zürich, Switzerland).

DISCUSSION

It has been clearly shown that not only the viscosity of the contents of a tube but also the design of the tube itself are important for the extrudability of the product. That different orifice diameters result in different outputs have earlier been shown by Wood and coworkers (5) and confirmed by our work, but we have also found that the tube width affects the extrusion. By squeezing a wide tube a larger amount of content is redistributed in the tube and pressed towards the tube walls and orifice, resulting in increased internal friction forces. On its way to the orifice its main part is stopped by the tube front and only a smaller part of the moving content is actually extruded. The friction forces involved in this process as well as the energy required to break the structure of the toothpaste to exceed its yield value is of course greater for a large tube than for a small one. One conclusion must be that the tube and content cannot be looked upon separately but should be regarded as a unit. A change in either of them results, from a rheological point of view, in a new product for which new squeeze tests must be done. Different degrees of annealing of the tube material has not been studied. Standard tubes were used, supplied by our tube manufacturer, who assured us that the annealing of the tube materials were the same.

A natural follow-up of this investigation would be a panel test to establish what squeeze time and squeeze force the consumer can accept, and how much toothpaste he wants on his brush. Simple laboratory tests will then determine whether the product will be acceptable for squeezing. A small panel test among our laboratory staff indicated that the amount of toothpaste used to brush the teeth is about 1.4 g (range 0.8–1.9 g), which corresponds to about one millilitre.

A serious drawback with the squeeze equation as it is now expressed is that one of the parameters used is the squeeze number. It would have been much more satisfying if instead a more measurable parameter was used, eg the degree of filling. With the present equation one can only calculate the outputs for consecutive squeezes at fixed squeeze force and squeeze time. If the degree of filling was used instead the history of the tube could be neglected with knowledge of how much of the contents was already used.

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  80 000 Sh.L.U./g
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