

THE JOURNAL OF THE SOCIETY OF COSMETIC CHEMISTS

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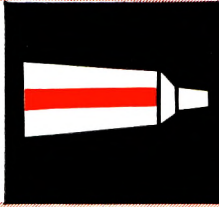


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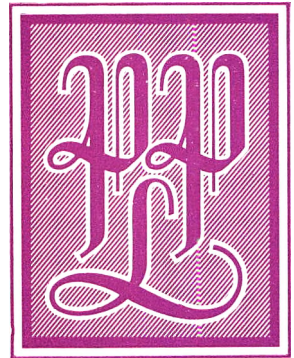


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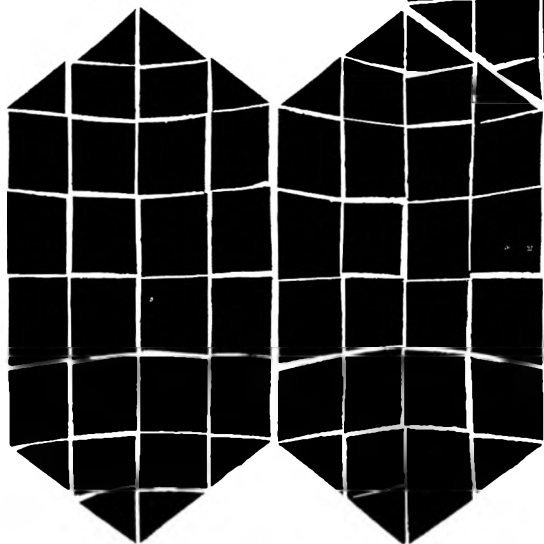
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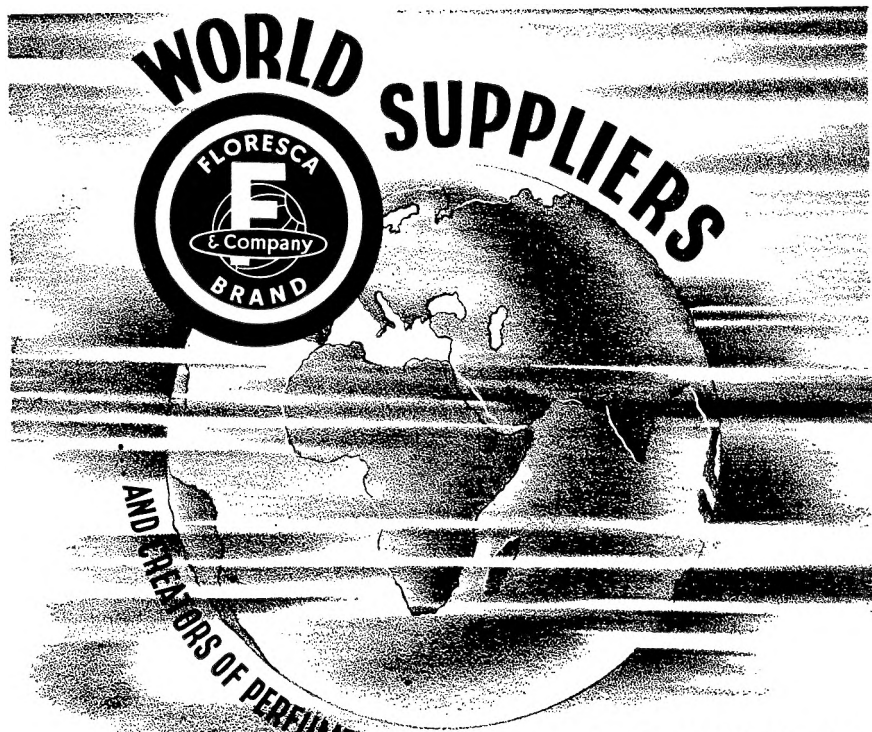


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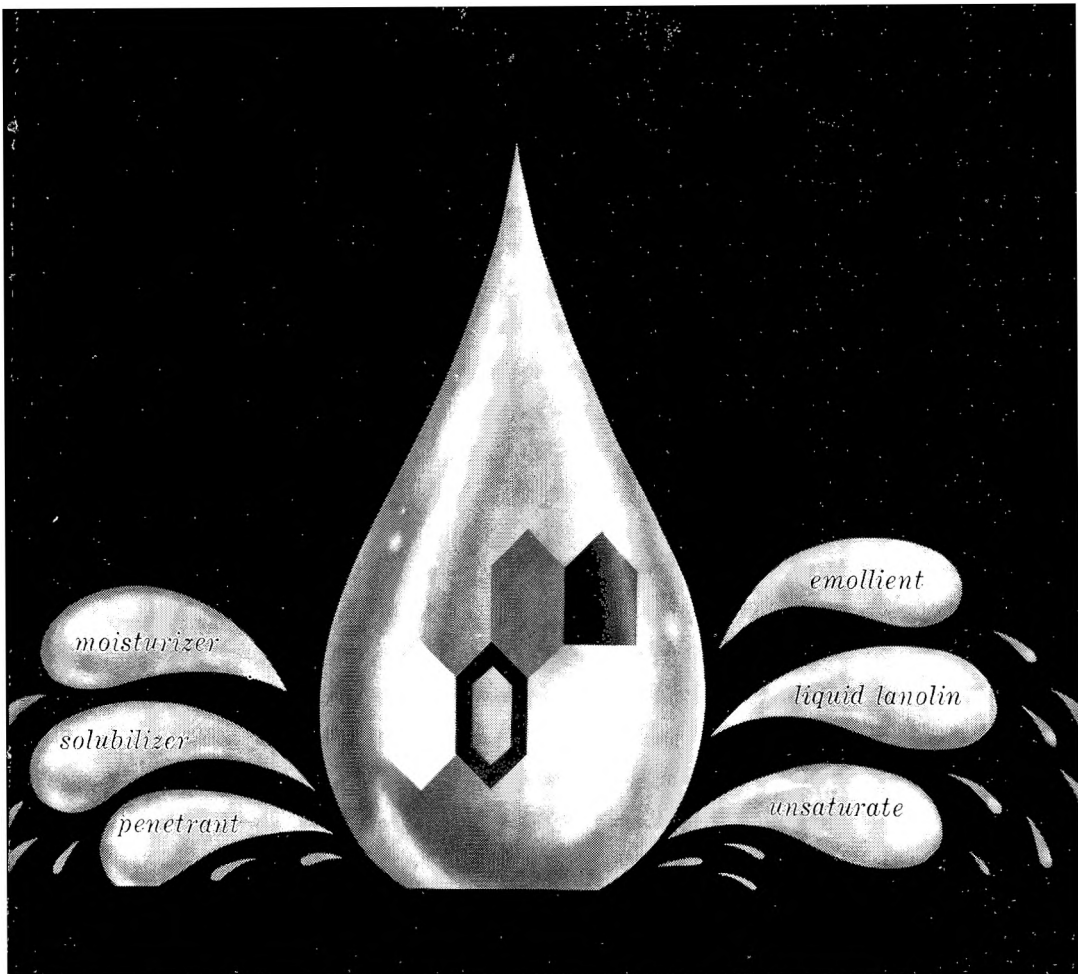
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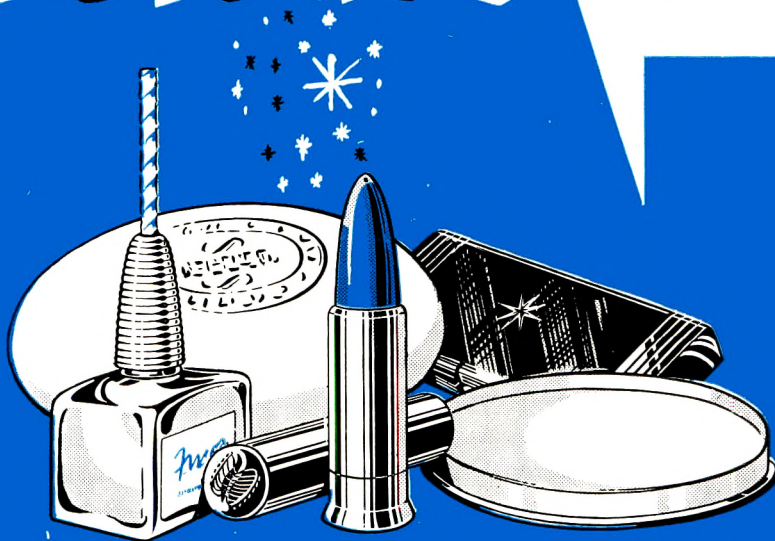
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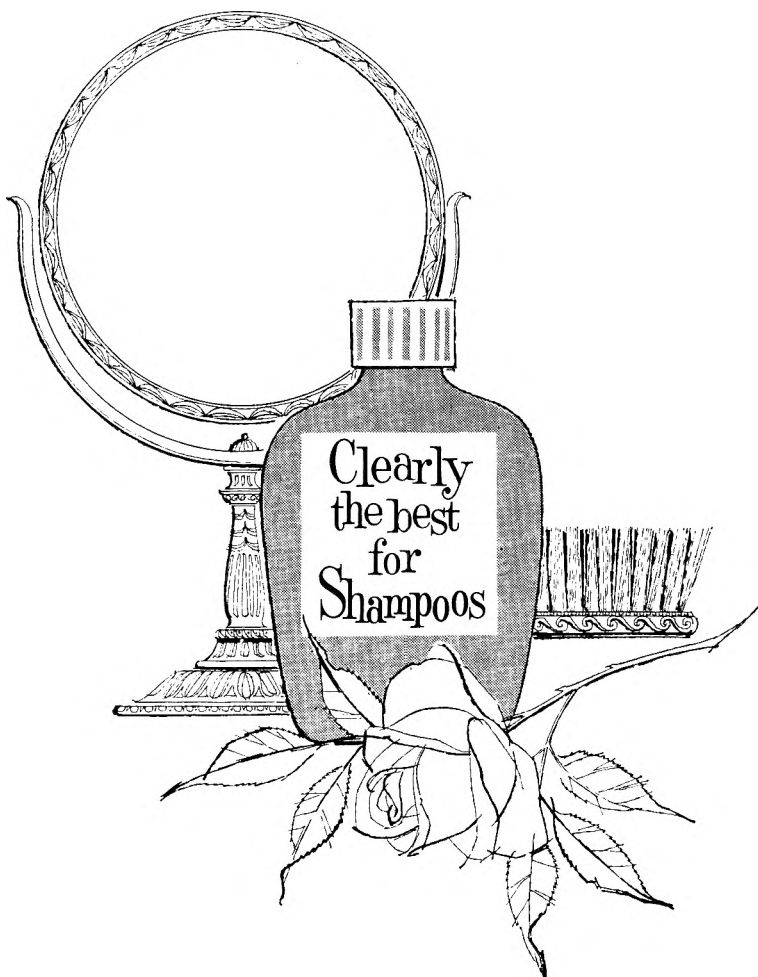
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SUMMARIES FOR CARD INDEXES

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

Hair lacquer systems and their evaluation: R. C. HARRIS. *Journal of the Society of Cosmetic Chemists* **14** 469 (1963)

Summary—The various ingredients, propellants, valves and containers, used for aerosol hair lacquers and the general principles of formulation in all its aspects are discussed, as are water-based aerosol hair lacquer systems. Typical formulations are given, and methods of laboratory evaluation and their limitations are discussed. Reference is made to the problems of toxicity and flammability.

Flammability of propellants: K. DIXON. *Journal of the Society of the Cosmetic Chemists* **14** 491 (1963)

Summary—Possible types of accidents with aerosols in the user's hands are considered. A method for assessing the fire risk associated with a bursting dispenser is described. Results obtained from this method and from flame extension tests are compared with some published figures. It is shown that any fire hazard is associated with the completed dispenser rather than with any particular ingredient.

Modern cosmetics—illusion and reality: T. J. ELLIOTT. *Journal of the Society of Cosmetic Chemists* **14** 503 (1963)

Summary—Despite improvements in modern cosmetics, many products still cause disappointment to the woman user.

Reasons for the discrepancy between advertising promise and product performance are discussed.

The analysis of synthetic detergents: W. B. SMITH. *Journal of the Society of Cosmetic Chemists* **14** 513 (1963)

Summary—The subject is introduced with a classification of surface active agents that are used in all types of detergents. This is followed by a review of the older qualitative tests and then an outline of a new paper chromatographic procedure. Quantitative analysis, confined to the determination of the active constituents, is described under headings of solvent extraction, colorimetric determination, anionic-cationic titration, and miscellaneous methods.

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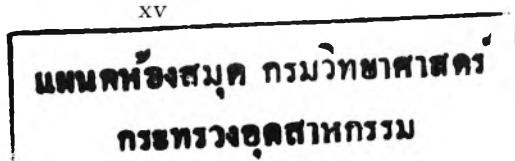
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VOL. XIV

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10

HAIR LACQUER SYSTEMS AND THEIR EVALUATION

R. C. HARRIS*

Presented at the Symposium on "Aerosols", organised by the Society, at Southport, Lancs., on 24th April 1963.

The various ingredients, propellants, valves and containers, used for aerosol hair lacquers and the general principles of formulation in all its aspects are discussed, as are water-based aerosol hair lacquer systems. Typical formulations are given, and methods of laboratory evaluation and their limitations are discussed. Reference is made to the problems of toxicity and flammability.

HAIR SETTING lotions based on water-soluble gums of vegetable origin have been used for many years, but the rapid-drying hair lacquer is a comparatively recent development. Its use was fairly limited until the advent of the aerosol pack which provided a simple and efficient means of applying this type of product. The aerosol hair lacquer first appeared in the U.S.A., in 1949, and today, in most countries, its sales exceed those of any other type of pressurized product. However, currently in several countries, the innocuity of the inhaled lacquer spray is being questioned and the flammability characteristics of hair lacquers (and other products) are being investigated critically, so any consideration of hair lacquer systems must pay due attention to these aspects.

*Swallowfield Aerosols Ltd., Wellington, Somerset.

The conventional pressurized hair lacquer consists basically of an "anhydrous" alcoholic solution of a film former, together with a chloro-fluorohydrocarbon propellant system, whereas the so-called water-based product, now appearing in significant numbers, employs an aqueous alcohol as the solvent and a hydrocarbon propellant system. In both types, other ingredients such as auxiliary solvents, plasticizers, perfumes, corrosion inhibitors, "conditioning" agents and spirit denaturants may be included. The composition of the "concentrate", i.e. the solution of film former and other ingredients, the type of propellant system, the ratio of propellant to concentrate, and the type of valve used, are the four critical factors which together determine the performance of the complete hair lacquer.

The hair lacquer is a surface coating product and whilst some formulation and laboratory evaluation problems are similar to those encountered with paints, there is one significant difference—the substrate to which the hair lacquer is applied. Not only do the natural characteristics of hair vary considerably from individual to individual, but the hairs may also be damaged or modified by bleaching, permanent waving, or by the use of rinses. The hair shafts vary in thickness and have an irregular surface "lubricated" with sebum, which is a varying mixture of fats, fatty acids, hydrocarbons, sterols, inorganic and organic salts.

Apart from these varying properties of the substrate, none of which would commend themselves to a paint technologist, there is also the problem created by the ultimate user. The lacquer will be sprayed from varying distances despite explicit instructions on the dispenser, and, similarly, the quantity applied will vary sharply. It is not surprising, therefore, that laboratory evaluation of hair lacquers must be supplemented by user trials despite their limitations.

LABORATORY EVALUATION

There are a number of factors governing the efficacy of hair lacquer which can be evaluated in the laboratory. These procedures can be used for quality control purposes, and for the initial screening and comparison of new formulations. Tests on locks of hair give valuable information, particularly regarding ease of combing and the tendency to flaking or stripping of the lacquer film.

The primary purpose of a hair lacquer is to hold the hair in the desired position, which is achieved by the stiffening effect of the film former which will be modified by the presence of other ingredients such as plasticizers, perfumes, lanolin derivatives, etc., and also by the humidity of the atmosphere. The stiffness or holding properties of the hair lacquer may be checked by several methods. Switches of hair which have been set into curls by water, dried and then sprayed, can be suspended in a controlled

humidity chamber, and the degree of return to the original shape measured. The Shirley Cloth Flexometer^{1,2}, which measures the degree to which strips of material, secured at one end, bend under their own or added weights, may be used for comparing the degree of stiffness imparted by various lacquers. Strips of filter paper (Whatman No. 41) or other suitable materials are impregnated with standard amounts of lacquer, dried and tested. The same procedure can be carried out at varying levels of humidity. The deposition of hair lacquer on "living" hair is somewhat uneven, depending upon a variety of factors such as distance and duration of spraying, and degree of penetration, but, nevertheless, these methods of comparing stiffness provide useful data.

A further important requirement is that the lacquer shall impart gloss or sheen to the hair. The gloss meters and reflectance spectrophotometers used in the paint industry are of little value for measuring the gloss of a lacquer film on hair, because of the variations in colour, texture and surface characteristics. Tests for gloss must, therefore, be conducted visually either on switches of hair or on living subjects. The spraying of hair lacquer on to glass plates will, however, reveal basic faults in the formulation giving cloudy or hazy films.

Many of the film formers used in hair lacquers are hygroscopic and since they are plasticized by water, the lacquer film will not only soften but may exhibit the highly undesirable property of tackiness. A simple method of measuring tackiness is to determine the weight which has to be applied to a piece of aluminium foil to make it adhere to a lacquer film on a glass plate, so that on inverting the plate, it will not fall off³.

The standard laboratory procedures are used for determining particle size, spray pattern, discharge rates and pressures.

FORMULATION OF CONCENTRATE

Solvents

Ethyl alcohol (Industrial Methylated Spirits 74 o.p.) is almost invariably used as the basic solvent for hair lacquers, although *isopropyl* alcohol, with its less severe corrosive properties, lower cost and freedom from Customs and Excise regulations in respect of denaturants, is used to a limited extent. Its odour, however, militates against its use except for products where cost is the prime consideration. The Customs and Excise Authorities require the addition of denaturants to the product, except in the case of shellac-based hair lacquers containing not less than 6 oz of shellac per Imperial gallon (i.e. concentrate excluding propellants). One or more of the following may be stipulated: Solution of quassin, diethyl phthalate, *Cetrimide*, sucrose octa-acetate, *Eitrex* solution. For conventional hair lacquers, the manufacturing and loading processes must be carried out with stringent care to

keep the water content to a minimum. Certain film formers, such as *Devlex A.515*, may require the addition of methylene chloride or 1,1,1-trichloroethane to the alcohol. Methylene chloride may also be used to prevent precipitation of the film former, and other ingredients, when chilled concentrates are used for cold-filling. Methylene chloride may cause damage to painted, lacquered or plastic surfaces if the sprayed lacquer impinges upon them.

For water-based lacquers, Industrial Methylated Spirits diluted with de-ionized water is used.

Film Formers

The ideal hair lacquer should provide a set, without tackiness, which will be maintained under varying conditions of humidity. It should impart gloss and a good "feel" to the hair, should have good adhesion and not flake off. The film should be sufficiently water-soluble to permit re-combing, and also removal by washing. No film former will meet these requirements fully and although some of the more recently introduced resins show improvements in some respects over the old established products, it is still necessary to incorporate modifying agents into the formulation to minimise or eliminate undesirable properties.

A wide variety of film formers have been tested, but most have proved unsuitable in some respect. Instability of colour, odour, corrosion problems, skin irritation and poor solubility in suitable solvents, are some of the causes for rejection. The development of new film formers for hair lacquers may now be retarded, as the screening for toxicity of inhaled spray particles will have to be carried out over long periods.

For the conventional hair lacquer the film former should be soluble in anhydrous ethyl alcohol (Industrial Methylated Spirits 74 o.p. is used) and in the final alcohol/propellant system. For water-based hair lacquers the film former must be soluble in 50-60% ethyl alcohol. It has been mentioned above that auxiliary solvents, such as methylene chloride may be used where the solubility in alcohol, particularly at low temperatures, is inadequate. The concentration of film former varies with the type and the particular purpose for which the hair lacquer is marketed, but it is usually within the range of 2.5-10% in the concentrate.

There is an extensive literature dealing with the chemical and physical properties of film formers used in hair lacquers, which also gives details of large numbers of formulations. It is, therefore, only necessary to summarize these details hereunder.

Shellac

The first film former to be used in pressurized hair lacquers was shellac which, although it does not fulfil many of the requirements quoted above,

notably in respect of ease of removal, is still used on a large scale, partly because of its cheapness, but also because the very stiff set which it can produce is useful for the upswept coiffure, and is frequently preferred by the professional hairdresser.

The shellac should be fully dewaxed, and a light coloured grade used. Shellac bleached by chlorine should not be used as it may give rise to corrosion problems. Bulk shellac should be stored in air-tight containers at as low a temperature as possible.

Unplasticized films of shellac are stiff and brittle, and rupture relatively easily on the hair, but are still difficult to remove by washing. Glycols, polyethylene glycols and their esters, are used to plasticize the film and aid in its ultimate removal. Phthalates and castor oil may also be used as plasticizers. Lanolin derivatives and *isopropyl* myristate may be included as "conditioners" and softening agents, but compatibility should be checked carefully, particularly if the product is to be cold-filled.

I					
Castor oil	0.6%
Shellac (dewaxed)	1.8%
Industrial Methylated Spirits 74 o.p.	27.6%
Propellant 12/11 (50 : 50)	70.0%

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<i>iso</i> Propyl myristate	0.7%
Shellac (dewaxed)	2.7%
Perfume	0.5%
Industrial Methylated Spirits 74 o.p.	31.1%
Propellant 11/12 (50 : 50)	65.0%

Ethyl Cellulose

Ethyl cellulose can be used for the water-resistant type of lacquer and a number of formulations have been published⁴. It is often used in combination with the more hygroscopic film formers, such as polyvinyl pyrrolidone. Water-miscible plasticizers such as triethyl citrate, glycerol or diethylene glycol oleate are suitable, and improve the ease of removal by washing.

III					
Ethyl cellulose T.10	2.0%
Diethylene glycol oleate	2.0%
*Absolute alcohol	46.0%
Propellant 12	50.0%

IV

Ethyl cellulose N.10	0.6%
Diethylene glycol oleate	0.7%
Polyvinyl pyrrolidone	0.7%
*Absolute alcohol	28.0%
Propellant 11	35.0%
Propellant 12	35.0%

*Formulations of U.S. origin quote either SDA-40 alcohol or absolute alcohol. Industrial Methylated Spirits 74 o.p. is used in the U.K.

Polyvinyl Pyrrolidone (PVP)

Originally used as a blood plasma extender, PVP came into use for pressurized hair lacquers in the early 1950's. It fulfils most of the requirements for a film former for hair lacquers. It is soluble in water, alcohol and alcohol/propellant mixtures, but it has the disadvantage of being hygroscopic. As supplied, it contains about 5% water, but the equilibrium moisture contents of films at 50% and 75% relative humidities are 17% and 25% respectively. Although dried films of PVP are glossy, transparent and hard, water plasticizes the film, causing softening and tackiness which is a disadvantage as the greatest need for a hair lacquer arises when conditions of high humidity prevail.

The incorporation of some plasticizers not only improves the flexibility of the PVP film, but also reduces hygroscopicity. Oleyl alcohol, glyceryl monoricinoleate, *Citroflex A-2* and dimethyl phthalate (10–25% based on the resin solids) are suggested. Lanolin derivatives serve a similar purpose⁵. Silicone fluids also reduce hygroscopicity when added at a rate of from 1–10% on the PVP content of the lacquer. Film formers such as shellac, dimethyl hydantoin formaldehyde resin and ethyl cellulose, added at approximately 10% of the PVP content, stiffen the film and render it less hydrophilic.

V

PVP	2.2%
Diethyl phthalate	0.4%
<i>iso</i> Propyl myristate	0.6%
Shellac (dewaxed)	0.3%
Perfume	0.5%
Industrial Methylated Spirits 74 o.p.	26.0%
Propellant 11/12 (50 : 50)	70.0%

VI

PVP	2.35%
Lanolin derivative	0.30%
Diethyl phthalate	0.65%
Silicone fluid	0.30%
Perfume	0.50%
Industrial Methylated Spirits 74 o.p.	60.90%
Propellant 12	35.00%

Vinyl Pyrrolidone/Vinyl Acetate Copolymers (PVP/VA)

The copolymers of vinyl acetate with vinyl pyrrolidone⁶ have film forming properties similar to PVP, but the vinyl acetate confers a greater degree of water resistance and reduces the solubility in water. The 60/40 vinyl pyrrolidone/vinyl acetate copolymer is commercially available. Although the PVP/VA films are less hygroscopic than PVP, they are, nevertheless, still somewhat hygroscopic and the addition of modifying agents similar to those used for PVP is necessary. The copolymers films are stiffer than corresponding PVP films, but additional film formers such as shellac, DMHF resin or ethyl cellulose may be added, as with PVP.

Hair lacquer formulations based on PVP/VA are of a similar type to those in which PVP is used.

Vinyl Acetate Copolymer

An acidic vinyl acetate copolymer, *National 28-1310*⁷, provides a resin which can be modified, by neutralisation with bases, to give films of differing degrees of flexibility and sensitivity to water. The preferred base is 2-amino-2-methyl-1, 3-propanediol and as the degree of neutralisation increases, the films produced become softer and more water-soluble. 85—95% neutralisation of the theoretical acidity produces a film of suitable characteristics.

The following formulae are suggested as a basis for experiment⁸ :—

VII

<i>National 28-1310</i>	3.45%
2-amino-2-methyl-1, 3-propanediol	0.38%
Alcohol soluble lanolin	0.90%
<i>iso</i> P-opyl myristate (cosmetic grade)	0.40%
Dipropylene glycol	0.10%
Perfume oil	0.35%
SDA-40 alcohol (anhydrous)	94.42%

VIII

<i>National 28-1310</i>	2.40%
2-amino-2-methyl-1, 3-propanediol	0.22%
Water soluble lanolin	0.10%
Silicone 555	0.10%
Perfume oil	0.40%
SDA-40 alcohol (anhydrous)	96.78%

Fill :

30% Concentrate

70% Propellant mixture

Acrylic Resins

Acrylic resins modified so that they are soluble in water, and suitable for hair lacquers, are described in two patents^{9,10}. The films have the clarity characteristic of this type of resin, are not hygroscopic, and are compatible with a wide range of plasticizers, lanolin derivatives and silicone fluids.

A typical formula is :—

IX

Modified acrylic resin	2.0%
Alcohol soluble lanolin	0.1%
Silicone fluid	0.1%
Perfume	0.5%
Industrial Methylated Spirits 74 o.p.	37.3%
Propellant 12/11 (50 : 50)	60.0%

Dimethyl Hydantoin Formaldehyde Resin (DMHF)

DMHF is a clear resin, soluble both in alcohol and in water, and gives a film which is slightly hygroscopic. It is compatible with other film formers including shellac, ethyl cellulose, PVP and PVP/VA copolymers. Lanolin derivatives and silicones may be incorporated into DMHF lacquers, and suitable plasticizers include polyethylene glycol 400 monolaurate, phthalates and glycols.

A suggested formula is¹¹:—

X				
DMHF resin, refined grade	5.0%
Liquid lanolin fraction	0.5%
Polyethylene glycol 400 monolaurate	0.5%
Perfume	1.0%
Anhydrous alcohol	93.0%

Fill :—

40% Concentrate (above)

60% Propellant

Devlex A.515

This resin, at present being produced in experimental quantities only, is a 50/50 copolymer of N-vinyl-5-methyl-2-oxazolidone and vinyl acetate¹². It produces clear films with a low degree of hygroscopicity. It is compatible with a variety of plasticizers, lanolin derivatives and silicone fluids, but requires the use of 1,1,1-trichloroethane or methylene chloride, in conjunction with ethyl alcohol to produce a satisfactory product.

Toxicity of Film Formers

Although the synthetic film formers described above have been subjected to extensive toxicity tests, the long-term effects of inhaled particles are now being questioned, and a brief survey of the position is given below.

The first report of pulmonary thesaurosis, alleged to result from the inhalation of hair lacquer spray particles, was made by Bergmann *et al*¹³ in 1958. In the same year, pulmonary alveolar proteinosis was reported by Rosen *et al*¹⁴, and a further case was reported by Edelston¹⁵. Calandra and Kay¹⁶, and Draize and his colleagues¹⁷, were unable to produce a comparable inhalation disease in animals using PVP, PVP/VA, DMHF, shellac, modified acrylic resin and lanolin.

Bergmann¹⁸ has since reported twelve new cases of thesaurosis, whilst Schepers¹⁹ has suggested that some cases of alleged thesaurosis may be sarcoidosis. However, the problem of toxicity is now being investigated in many quarters, but whatever the outcome of these investigations, any modification of formulation or of valve design which reduces the possibility of inhalation of the sprayed lacquer is a progressive step.

Plasticizers and Modifying Agents

None of the resins developed so far for hair lacquers is ideal, and the

addition of plasticizers or softeners is necessary to control the flexibility, adhesion, gloss, clarity and moisture sensitivity of the film. Many ingredients used in hair lacquer formulations possess plasticizing or softening properties, although they may be included in the formulation to fulfil other functions. Lanolin derivatives, cetyl and oleyl alcohols, *isopropyl* myristate and other similar materials used as hair "conditioning" and spreading agents, may act as softeners or true plasticizers. Perfumes, which may be present in concentrations as high as 20% in relation to the resin content, contain essential oils, esters, ketones, alcohols, etc., and their plasticizing or softening effect may be considerable. Silicone fluids, included to increase water repellency, lubricity and gloss, act similarly. Since the addition of true plasticizers is also necessary, the combined plasticizing effect of the various ingredients must be carefully checked to ensure that the final film is satisfactory in all respects.

It is not only necessary to check that the final concentrate and propellant are compatible, but also to ensure that, during the drying of the film, there is no gelling or precipitation of any individual ingredient which will result in a lustreless film of poor adhesion. This applies particularly to the water-based product where the solvent composition changes sharply as the film dries.

Some ingredients function as softeners rather than as true plasticizers and may exude from the film, which may or may not be desirable because, although the exudate may act as a lubricant and impart anti-static properties, it may also render the film dull.

Examples of the types of plasticizers used with various film formers have already been given, and it is only necessary to state the general principles underlying the choice of a plasticizer, which are governed by the physical properties of the resin concerned, and by the properties required of the final film. With the more hygroscopic resins, water-miscible and humectant plasticizers should either be avoided or used in very low proportions. Glycols increase the tackiness of PVP films sharply. For the water-resistant resins, water-miscible plasticizers such as diethylene glycol oleate, triethyl citrate, and glycols may be used.

Plasticizers, or modifying agents with surface active properties, will assist in the spreading of the hair lacquer over the hair. This property is more important with the water-based product because of the higher surface tension of the deposited droplets.

An interesting class of "stiffening" agents for pressurized hair lacquers has been described²⁰. The incorporation of certain substituted benzophenone derivatives, particularly 2,2',4,4'-tetrahydroxybenzophenone, is reported to increase markedly the stiffness of hair lacquer films.

PROPELLANT SYSTEM

The pressurized hair lacquer is a surface coating product, and so the quantity and composition of the propellants used must produce a relatively coarse spray, in conjunction with the particular valve used. This aspect has now assumed greater importance because if inhaled spray particles do constitute a health hazard, then the danger increases as the particle size decreases. Several other major considerations, including flammability characteristics, corrosion problems and cost, also govern the choice of propellant system.

The chlorofluorohydrocarbon propellant systems used for hair lacquers usually consist of a mixture of propellants 11 and 12, or propellant 12 alone. Methylene chloride and 1,1,1-trichloroethane are also used in conjunction with propellant 12, serving both as solvents and pressure depressants. A combination of propane and propellant 11, referred to below, has not, so far, been used in Great Britain, largely because the odour of the propane available has been poor, although it is now improving.

The ratio of propellant 11 to propellant 12 may be varied, although the 50/50 mixture is most frequently used, partly because of economic considerations. By increasing the proportion of propellant 11 to propellant 12, the internal pressure of the pack is reduced and a wetter spray of larger average particle size results. The refillable "mother and daughter" packs normally contain a propellant mixture having a preponderance of propellant 11, as the necessary over-pressurizing of the "mother" pack with nitrogen may otherwise create pressures which are too high for safety, particularly as a larger can is used for the "mother" pack. It might be noted here that the refillable "daughter" pack must be thoroughly purged of air.

The use of propellant 12 alone reduces some of the problems of compatibility and perfume stability. It also has the dubious advantage of giving the purchaser the impression that the pack contains a greater quantity of product, as the volume occupied by a 65% concentrate/35% propellant 12 fill is about 15—20% greater than that occupied by a product containing 35% concentrate and 65% of a propellant 11/12 mixture.

FLAMMABILITY

The flammability of hair lacquers is under investigation, but having regard to the vast number which have been produced and used, without mishap, it may well be that the danger is exaggerated. Nevertheless, the formulator of a pressurized hair lacquer must consider this aspect carefully, and choose the least flammable formulation consistent with efficiency.

The methods employed for testing the flammability of pressurized products, and the interpretation of the results obtained thereby are, themselves, the subject of controversy. However, the aerosol industry throughout the

world uses the C.S.M.A. methods²¹, which provide a valuable means of comparing the flammability hazards of various formulations. Felton and Yeomans²² recently suggested an alternative method, using a 12 oz drawn steel aerosol can as a combustion chamber, and a sparking plug as an ignition source.

The flammable nature of the solvents used in the conventional hair lacquer renders the use of flammable propellants, such as hydrocarbons and vinyl chloride, inadvisable except in limited amounts in combination with the chlorofluorohydrocarbon propellants 11 and 12. In the U.S.A., formulations containing propane and propellant 11 have been used. The formulation given below was tested by C.S.M.A. members²³, and the recommended classification was "nonflammable".

XI

<i>E. 735</i> (PVP/VA copolymer)	0.750%
Lanogene	0.060%
Silicone	0.030%
Perfume	0.165%
Absolute ethyl alcohol	13.995%
Propellant 11	77.000%
Propane	8.000%

If 80% by weight, or more, of a chlorofluorohydrocarbon propellant is used, even with highly flammable solvents, the flammability hazard is negligible due to the flame inhibiting properties of these compounds. This has been confirmed recently during tests carried out by Kempe²⁴. The ratio of propellant to concentrate will, however, produce a spray containing a high proportion of fine particles which is undesirable. A product containing 70% by weight of a mixture of propellants 11 and 12, and 30% of lacquer concentrate will give a flame projection of 9-10" when tested by the C.S.M.A. flame projection test, but as the ratio of propellant to concentrate decreases, the flame extension increases until a product containing 65% concentrate and 35% propellant 12 will produce a flame extension of almost 2'. It should be mentioned that the discharge rate, and the spray pattern influence these results.

For water-based hair lacquers, containing a film former dissolved in aqueous alcohol and pressurized by a hydrocarbon propellant, the flame extensions will be of the same order as the conventional 70/30 propellant/concentrate lacquer. Labelling as "non-flammable" was given by C.S.M.A. members²³ for the following basic formulation:—

XII

PVP	2.0%
Ethanol (absolute)			41.6%
Water	34.4%
<i>iso</i> Butane		22.0%

CORROSION

When a mixture of propellants 11 and 12 is used for a pressurized hair lacquer, the water content of the finished pack must be kept to a minimum to prevent the occurrence of serious corrosion. It was thought that the cause of the corrosion was due to the acid produced as a result of hydrolysis of propellant 11 until Sanders²⁵ showed that the major cause for the development of acidity was due to the reaction of ethyl alcohol with propellant 11. Following this discovery, further work carried out showed that nitromethane added at 0.3% to propellant 11 was an efficient stabiliser for this alcohol/propellant system^{26,27}.

The use of propellant 12 alone, usually at about 35%, considerably reduces the risk of corrosion, and many pressurized hair lacquers using this system are now being marketed.

It should be noted that aluminium containers used for any type of hair lacquer must be internally lacquered with a system giving 100% protection.

When tinplate containers are to be used for water-based hair lacquers, the internal protection of the container becomes of paramount importance. Details of the various lacquer systems used for the body and side seams of tinplate containers are given by Johnsen^{28,29}, and Garten³⁰.

Prolonged shelf tests are necessary for water-based hair lacquers, and test containers should be filled on a production basis as well as in the laboratory, because there are some factors not yet fully understood which affect shelf life. The amount of air present in the containers is certainly an important factor.

COST

The chlorofluorohydrocarbon propellants are expensive by comparison with the hydrocarbon propellants and, usually, unless the concentrate includes expensive perfumes or other ingredients, with the concentrate itself. Propellants 11 and 12 are normally used, as cost rules out the use of propellant 114, despite its advantages in some respects. The tendency to use high concentrate/low propellant ratios has been encouraged by the preponderance of pressure filling equipment available, and further economies result from the increased filling rates.

The water-based products offer not only the advantage of a cheaper propellant system but also of a cheaper concentrate, as about half of the ethyl alcohol used in the conventional hair lacquer is replaced by de-ionised water. The extra cost of internally lacquered containers, special valves, and the increased capital cost incurred as a result of the need for additional safety equipment for hydrocarbon filling, do not materially offset the saving. It might be noted that the somewhat slower drying time of these lacquers is not always preferred.

PROPELLANT/CONCENTRATE RATIO AND CHOICE OF VALVE TYPE

The particle size distribution, and the spray pattern, are dependent upon several factors including the surface tension and viscosity of the product, the ratio of propellant to concentrate, the type of propellant, and the type of valve used.

The higher the proportion of propellant in the emerging product, the greater is the volume of vapour formed and thus the greater is the degree of atomization. The higher the vapour pressure of the propellant used, the more rapid is the vaporization, and again the degree of atomization is greater. A hair lacquer based on 70/30 or a 65/35 propellant/concentrate ratio, using a standard valve actuator, will produce a suitable spray, but as the ratio of propellant to concentrate decreases, the spray becomes progressively jet-like and a valve with a mechanical break-up actuator must be used to produce a suitable spray. These actuators vary in design and some are more efficient than others, but the general principle of operation is the same. The exit of the liquid stream is mechanically impeded so that some of the kinetic energy of forward movement is used to disrupt the liquid mass. The jet which would be produced by a standard actuator is replaced by a relatively coarse spray of lesser forward velocity.

Figures 1—6 demonstrate the effect of the various combinations of propellant type, propellant/concentrate ratio, and valve actuator.

The spray pattern apparatus described by Gunn-Smith and Platt³¹ was used to record the spray patterns. The following basic concentrate, coloured with Gentian violet, was used throughout.

DMHF resin	6.25%
Larolin derivative	0.45%
Propylene glycol	0.45%
Perfume	0.75%
Industrial Methylated Spirits 74 o.p.	92.10%

The spray pattern shown in *Fig. 1* is suitable for all types of product, but is particularly useful for products where considerable holding power is required. The relatively narrow spray cone enables individual curls to be

treated easily, and the high velocity of the spray particles ensures penetration into the hair and also reduces "beading" on the hair shafts. The spray pattern shown in *Fig. 2* indicates a softer type of spray with less penetration, whilst that shown in *Fig. 3* is, perhaps, too diffuse. *Fig. 4* clearly shows the unsatisfactory pattern produced by the low propellant to product ratio, when a standard actuator is used. *Figs. 5* and *6* illustrate the effect of the mechanical break-up actuator on this formulation.

The use of low propellant to concentrate ratios means that the concentration of alcohol in the pack is greater, and the tendency towards stress-cracking of the valve diptube is increased. There could also be some hardening of the valve gasket, which may be significant with "mother and daughter" packs.

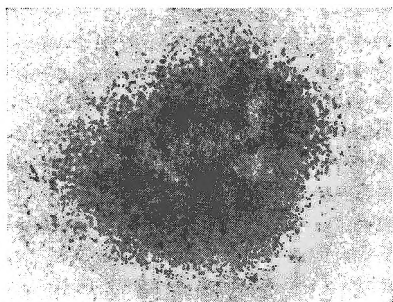


Figure 1

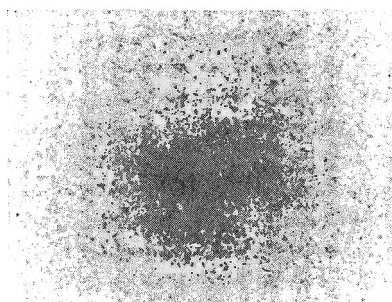


Figure 2

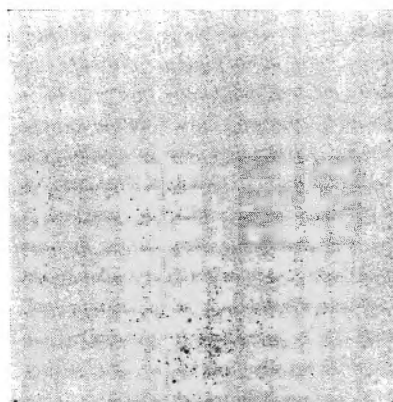


Figure 3

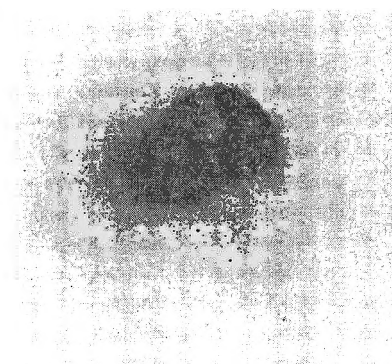


Figure 4

Figure	Concentrate Percentage	Propellant Percentage	Valve Actuator
1	35	65 (propellant 11/12 (50 : 50))	standard
2	35	65	mechanical break-up (type A)
3	35	65	mechanical break-up (type B)
4	65	35 (propellant 12)	standard

Spray distance : 8 inches
 Temperature : 70°F.

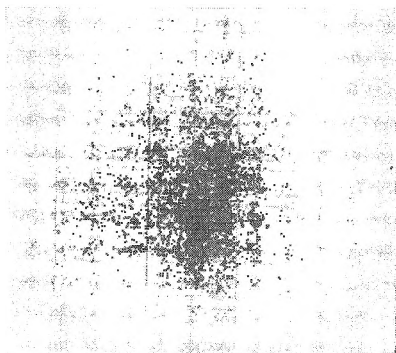


Figure 5

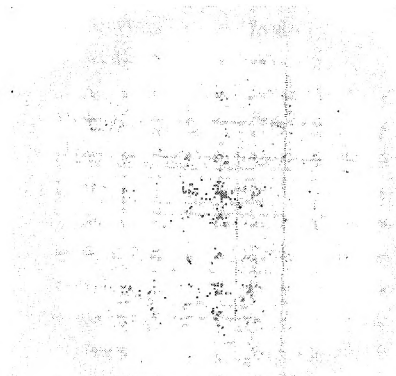


Figure 6



Figure 7

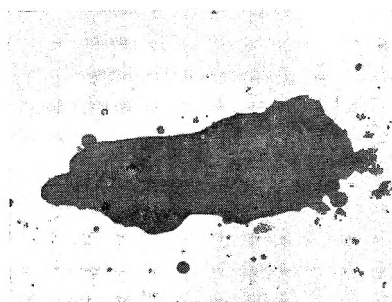


Figure 8

Figure	Concentrate Percentage	Propellant Percentage	Valve Actuator
5	65	35 (propellant 12)	mechanical break-up (type A)
6	65	35 „	mechanical break-up (type B)

Figure 7 shows the optimum result obtainable with the same formulation sprayed, from a polythene squeeze bottle, while Figure 8 shows the result which may be obtained from the same squeeze bottle, when it is improperly operated.

Spray distance : 8 inches

Temperature : 70°F.

The water-based hair lacquers require a special valve system to ensure a reasonable degree of atomization. The valve housing must have a vapour phase orifice, which permits propellant vapour to enter the housing thereby increasing the break-up of the liquid stream. The tendency of the propellant to vaporize in the diptube is reduced by the use of a capillary diptube. The valve actuator should be of the mechanical break-up type.

CONCLUSION

At present it is impossible to foresee what effect the present investigations into toxicity and flammability hazards will have on the future development of pressurized hair lacquers. Investigations into the physiological properties of film formers may prove enlightening, and film forming products which can be metabolized readily may be developed.

The present situation offers a challenge to the cosmetic industry which must be accepted.

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Introduction by the lecturer

The pressurized hair lacquer is the subject of more controversy than any other pressurized product. Toxicity and flammability hazards are the subject of critical investigation in many countries. It has been the

subject of more commercial failures than any other pressurized product, which have been due to a variety of causes, including corrosion of the container, deterioration of the product, incompatibility of the product with the propellant, valve failure through blockage, gasket hardening, and the falling off of the dip tube.

I would therefore like to stress the necessity for exercising rigid quality control of incoming raw materials, components, and of manufacturing and filling operations.

The alcohol and film formers must be handled with extreme care to prevent the uptake of water. Most of them, as supplied, contain a small and unavoidable amount of water. These amounts are not serious, but careless storage, processing, and filling can increase them to dangerous levels. The water content of the finished pack is critical, and may contribute to product deterioration and container failure.

Compatibility tests should be carried out on every incoming batch of raw materials, in addition to routine analyses for water content, etc. This is particularly important with shellac. Where cold filling operations are carried out, the minimum temperature to which the concentrate can be chilled without throw-out of the resins and other ingredients, should be carefully established, and plant control should be such that the concentrate is not chilled below this level.

If aluminium containers are used, then the integrity and efficiency of the lacquer system should be investigated most carefully. Routine tests, such as checks on the seams of tinplate containers, neck dimensions, and container strengths, must also be carried out.

Apart from general valve quality control, particular attention should be paid to the effect of the formulation on the rubber valve gasket. Since the hair lacquer formulations are active stress-raising agents, the possibility of environmental stress-cracking of the polyethylene dip tube used on each batch of valves must be checked. The interference fit constituted by the pushing of the end of the dip tube over the tailpiece of the valve housing in some valves creates a multi-axial stress system which may, especially if active stress-raising ingredients are present in the pack, result in longitudinal splitting of the polyethylene in this region, causing the dip tube to fall off the housing, and the pack to be useless. This has actually happened.

A suitable test method is to immerse the assembled dip tube and valve housing in a 2.5% solution of nonyl phenol ethylene oxide condensate (*Lissapol NX*), for 24 hours at room temperature. If no splitting occurs in the region of mating of the dip tube and valve housing tailpiece, the valves should be satisfactory for most conventional hair lacquer formulations. If, however, splitting does occur, then the valves must be rejected, re-tubed,

or used for formulations which have little stress-raising properties, if further functional tests prove satisfactory.

During refrigerated filling operations, the propellant and concentrate delivery nozzles should be kept clear of ice and water. When pressure loading is used, efficient purging or evacuation of the air from the container must be carried out.

I must stress that the uncompromising control of every aspect of manufacture is vitally necessary. Failure of a commercial product harms everyone in the industry, and not only the filler or marketer directly concerned.

DISCUSSION

MR. A. HERZKA : Thesauriosis of the lungs, allegedly due to hair lacquers, is now receiving a good deal of attention, and there is one aspect, briefly referred to by you, which I wish to stress. Although publications in the past have dealt mainly with the type of film formers, it could well be that the results of the various investigations now under way will indicate that the particle size of the spray is as, if not more, important than the nature of the film former. Many of the formulations cited in your paper employ propellant concentrations of 70%, and the resulting spray will be almost equal to that of an air freshener, with extremely small particles which remain suspended in the atmosphere for quite a time, and can thus be inhaled very easily. Such formulations are known to be employed in the United States in order to obtain a spray which is classified as nonflammable. In this country, however, it is doubtful whether there are many packs which employ a propellant concentration in excess of 50%. Consequently I believe that formulations with a low propellant concentration present far less of a hazard, if there is a hazard at all, than the packs utilising many of the formulations which you have listed.

THE LECTURER : A considerable proportion of the pressurized hair lacquers marketed in this country do contain propellant concentrations in excess of 50%. Considerations of flammability have prompted the use of formulations of this type.

The use of lower rates of propellant concentration obviously reduces the proportion of fine particles in the spray cloud and hence the number of fine particles inhaled.

Whilst the proportion of fine particles diminishes as the propellant concentration falls, there is still a significant proportion of particles of five microns or less. The use of a mechanical break-up actuator, which is necessary for formulations containing low percentages of propellants, results in a diffuse spray cloud of particles possessing lesser forward velocities, and hence the possibility of inhalation of particles tends to increase.

DR. H. KÜBLER : According to our experience a concentration of more than 20% methylene chloride can cause structural damage to the hair.

THE LECTURER : I have no direct experience with regard to damage of the hair by methylene chloride, but feel that its use in hair lacquer formulations is to be deprecated. Its effect on valve rubbers and polyethylene dip tubing needs careful evaluation, and it can cause high weight losses on storage. It is prone to hydrolysis, and has deleterious effects on some perfumes. As I mentioned, the falling spray can cause damage to the surfaces of furniture and fixtures.

A high local concentration of methylene chloride in the air space surrounding the user may result. Methylene chloride may have some effect on ciliary activity, which may increase inhalation hazards.

DR. H. KÜBLER : A good hair lacquer must be removable by washing. Can silicones be completely removed by washing, or do they accumulate in the hair ?

THE LECTURER : The percentage of silicones used in hair lacquers is relatively low, and I have not heard of any difficulty regarding the removal of hair lacquers containing silicone from the hair.

Laboratory tests with hair switches repeatedly sprayed with lacquer containing silicones, and washed between each spraying have given no indication of an accumulation of silicone.

DR. H. KÜBLER : In the matter of flammable propellants, I wish to state that my experience covers the production of many millions of hair lacquer, utilising vinyl chloride as the propellant. No accident directly attributable to this propellant has been reported.

THE LECTURER : I appreciate the fact that, despite the wide use of flammable solvents and propellants, there have been few accidents with conventional hair lacquers.

Nevertheless, since the actual concentrates are flammable and the use of flammable propellants aggravates the danger, I believe it is incumbent upon the formulator to develop the least hazardous product possible within limitations imposed by basic considerations of the performance of the product.

MR. J. WALLIS : In any system of product/propellant/container, there is a water concentration *below* which corrosion is just as severe as if the formulation is 'wet'. Thus the use of 75 o.p. alcohol, or specially dried resins, can cause severe corrosion which would not occur if 74 o.p. spirit were used.

THE LECTURER : The problem of "dry" formulations does not arise commercially. The alcohol and resins, as supplied, contain water, and it is

necessary to exercise stringent quality control of incoming materials, and of manufacturing and filling methods to prevent uptake of additional water.

The preparation of virtually "anhydrous" hair lacquer systems is a tedious laboratory procedure.

MR. P. MOXEY : What is the incidence of stress cracking in dip tubing? The use of butyl rubber additives in the polythene is not necessary as there are ethylene-butene and ethylene-propylene copolymers which are superior. The 24-hour method used by you to determine the possibility of stress cracking is an "accelerated test", which would come as news to the plastics industry, which has not yet been able to evolve such a test.

THE LECTURER : The incorporation of additives in the polyethylene used for dip tubing is a comparatively recent innovation in this country. The filler is entirely in the hands of the valve supplier in this matter, and has no choice with respect to additives.

The 24-hour procedure described is not an absolute test. The test solution is an active stress-raising agent, and the immersion of the assembled dip tube with the multi-axial stress system created by the interference fit where the dip tube is pushed over the valve housing tailpiece, provides a fairly severe test.

Long experience and collation of many thousands of results enable us to determine the suitability of the dip tube for a given product. On occasion the dip tube may be rejected, but in some cases whilst it may not be suitable for products with severe stress-raising properties, it could be perfectly satisfactory for products which have but little stress-raising properties. This is a matter of experience.

MR. N. BLACKMORE : In your paper a formulation involving the use of ethyl cellulose to improve water resistance is quoted. In my experience, this resin is so water resistant that it does not wash off the hair even with an alkaline shampoo. This is in contrast to shellac, a widely used water insoluble resin, which is removed with alkaline shampoo. Would you not agree that the extreme water resistance of ethyl cellulose films makes it unsuitable for use in hair lacquers?

THE LECTURER : Ethyl cellulose has never been widely accepted in this country, principally because of the difficulty of removal from the hair. It has been used to a limited extent in conjunction with the more hygroscopic resins to reduce the undesirable property of tackiness.

MR. N. BLACKMORE : Regarding denaturants, could you suggest a system which could be used with *National 28-1310*. As this resin cannot itself be regarded as a denaturant, two suitable denaturants have to be selected. Out of the list given in your paper one only may be selected from quassin,

sucrose octa-acetate or *Bitrex*, but what about the second? Diethyl phthalate tends to make the resin film over-plasticise and greasy, while *Cetrimide* causes corrosion. Other denaturants suffer also from serious drawbacks of one kind or another.

THE LECTURER : Customs & Excise Regulations require denaturants to render the spirit nonpotable. The denaturants must also be difficult to remove. Whilst general principles are laid down, the Customs & Excise will consider sympathetically any suggestions for alternative denaturant systems, if it can be clearly shown that the normal ones recommended are unsuitable. I agree that the use of diethyl phthalate and *Cetrimide* are open to objection for this type of product. A fair case could be made out for using alternatives, and two denaturants from the class mentioned might well be accepted. These matters are negotiable.

MR. R. E. ECKTON : It has been stated recently that 60% of hair lacquers which do not contain 0.3% nitromethane develop objectionable odours within two months. Could you please comment on this from your experience?

THE LECTURER : In my own experience this is not so. A vast number of hair lacquers containing propellant 11 have been on the market for many years, and I have never encountered a complaint that the perfume had developed an objectionable odour. We recently examined some hair lacquers packed in 1956 and subsequently stored at ambient temperature. These were still satisfactory in all respects, including the perfumes.

FLAMMABILITY OF PROPELLANTS

K. DIXON, B.Sc*.

Presented at the Symposium on "Aerosols", organised by the Society, at Southport, Lancs., on 25th April 1963.

Possible types of accidents with aerosols in the user's hands are considered. A method for assessing the fire risk associated with a bursting dispenser is described. Results obtained from this method and from flame extension tests are compared with some published figures. It is shown that any fire hazard is associated with the complete dispenser rather than with any particular ingredient.

THE AEROSOL industry is continually searching for a method of reducing the cost of its products, and it is well known that the use of flammable propellants in place of the conventional chlorofluorohydrocarbons would help in this direction—if it could be done safely. Practices differ from country to country. For example butane propelled aerosols, giving an extensive flame when ignited, are common in France, and in Germany we believe opinions to be divided, with some interest in the use of vinyl chloride.

Since the end of 1961, a leading marketer in the U.S.A. has apparently made a success of products depending on a butane/water emulsion as propellant and in doing so has precipitated a major controversy with regard to their safety.

In this country we are trying to decide, on the evidence available, what are the risks in using a flammable propellant *per se*.

In this paper the evidence is reviewed and the possible hazards in the user's hands have been considered. Possible hazards existing in the manufacture and bulk storage and transport also require careful consideration, but are beyond the scope of this paper.

As little information on accidents appeared to be available, a review has been made of relevant incidents covering 12 years' experience, and the sale of over 70,000,000 aerosols. As a result of this review, a method of testing the fire hazard associated with a bursting dispenser was developed and this is described below. The results obtained are compared with those obtained by some of the standard C.S.M.A. methods, and with some published results from the literature. It is concluded that the most likely hazard in which fire may be involved is explosion of a dispenser due to mis-use, and that the intrinsic fire risk associated with a dispenser is more properly related to the

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total amount of flammable material contained in it than to the specific nature of the flammable material concerned.

REVIEW OF ACCIDENTS

During the period under review (1950—1962) our Company has sold over 70,000,000 aerosols, the majority direct to the consumer market, with others on a contract filling basis. This has given us some sight into consumer reaction, not only towards our own products but also towards a wide range of other types. The bulk of them have been distributed within the United Kingdom, but a proportion have been exported to many parts of the world, including most climatic and cultural conditions. In response to a questionnaire sent out, covering accidents involving fire or explosion, we obtained reports of four relevant incidents, which were as follows :

- (a) A 20 oz insecticide pressure pack was placed in the steam from a boiling kettle, and exploded. There were, fortunately, no injuries nor fire.
- (b) A 6 oz insecticide pressure pack was placed on a domestic boiler. The ends inverted. There was neither fire nor explosion.
- (c) A 6 oz insecticide pack was exposed to strong sunlight in a shop window, and exploded. There was no fire.
- (d) A 12 oz insecticide left in strong sunlight in the back of a car failed at the sideseam. There was no fire.

In addition to these specific reports, we have information from a few tropical or semi-tropical countries, of explosions occurring due to exposure either to sunlight or to other forms of heat. We have not been able to obtain any reports of accidents involving fire where the contents of an aerosol were the first material ignited, nor of any where, in the hands of a consumer, an aerosol has contributed effectively to a fire.

During most of the period under review we have been selling, as a significant proportion of the total, a product containing over 50% w/w of flammable material, and giving a flame extension by the C.S.M.A. method of about 20". Products with similar fire characteristics have been widely marketed in this country for the last eight or ten years, and to the best of our knowledge no accidents involving fire have occurred. We can only conclude that these products, which bear legends such as "Do not spray near a naked flame or while smoking" are safe in a consumer's hands.

The fact that few accidents have occurred in the hands of users would suggest that aerosol products are reasonably safe, and we are left with the two questions "Are those propelled by a butane-water emulsion any less safe?", and "In what way, if any, are they less safe?".

There appear to be three reasonable sources of hazard :

- (a) Ignition of the spray during use of the dispenser ; this is covered by the flame extension test.
- (b) Explosion of the dispenser under extreme conditions, and
- (c) Possible leakage of flammable materials from damaged or defective units.

Taking these in reverse order, we consider that the evidence available shows that leakage from a pressure pack presents no greater hazard than that from other common household articles. From past experience, the risk of explosion and subsequent fire appears to be the greatest and a test method for this, together with some results, is described below. Flame extension tests are discussed subsequently.

BURST/FIRE TEST

The apparatus for this test consists of a cylindrical steel brazier and a surrounding frame. The brazier is 1' in diameter and 1' 3" high. It has a closed base, air vents through about a quarter of the surface of the upper half of the cylinder, and a grid over the top. The frame is 6' in diameter, and arranged symmetrically around the fire. To it is fixed a cylinder of cretonne cloth, 6' in diameter and 4' high, with its base 2' above the ground.

The lower half of the brazier is filled with a slurry of *isopropyl* alcohol and sand, which should just not have liquid showing free on top. This mixture is ignited and when burning well, the dispenser under test is placed centrally on the grid with its axis horizontal.

A positive result is recorded if, on the explosion of the dispenser, the cretonne "curtain" is ignited, a negative result if it is not. Care should be taken to ensure that the sand/*isopropyl* alcohol slurry is not sufficiently fluid to be blown about by the explosion, and so confuse the results.

A gas-ring has been tried as an alternative source of heat but was abandoned as it was frequently extinguished by the force of the explosion, without having ignited the contents of the dispenser.

A series of tests using this apparatus has been carried out employing 6 oz, 8 oz, 12 oz, and 16 oz tinplate containers. In so far as was practicable each size of container was filled with 10 g, 20 g, 40 g, 80 g and 160 g commercial butane (about 55% *n*butane, 35% *isobutane* and 10% propane) together with sufficient water or odourless kerosene, or 50/50 w/w water/*methylated* spirit mixture, to leave approx. 20% ullage in the container at 70°F. The filling weights are given in *Table 1*, and the results of the tests in *Table 2*. These are presented in fractional form, the upper figure being the number of

Table 1

Filling weights in gram, of dispensers used in Burst/Fire tests.

Solvent	Nominal container size	Amount of butane				
		10 g	20 g	40 g	80 g	160 g
Odourless kerosene	6 oz	119.6	116.5	110.2	97.6	—
	8 oz	179.4	176.3	170.0	157.4	—
	12 oz	233.0	230.0	223.5	211.0	185.8
	16 oz	318.0	314.8	308.5	296.0	270.8
50% w/w Water 50% w/w Methylated Spirits	6 oz	135.6	130.6	120.5	100.2	—
	8 oz	204.2	199.1	189.0	168.6	—
	12 oz	265.5	260.4	250.2	230.1	189.6
	16 oz	363.0	357.9	347.8	327.5	287.0
Water	6 oz	149.3	142.6	129.2	102.4	—
	8 oz	225.3	218.6	205.2	178.4	—
	12 oz	293.3	286.6	273.2	246.4	192.8
	16 oz	401.3	394.6	381.2	354.4	300.8

curtain fires occurring, and the lower the number of dispensers tested. It was felt that an adequate picture could be built up by taking selected values of the variables. Ten containers have therefore been tested at the selected values, and one or two at other values. Only those results on groups of ten containers are analysed further.

The mean proportion by weight of flammable material (this includes odourless kerosene for the present purpose) has been calculated for each group of dispensers giving 0 out of 10 fires, 1 out of 10 fires, etc., and plotted against the proportion of fires in *Figure 1* where the resulting line is shown solid.

Similar results have been obtained on widely marketed Arcton-propelled products containing 20%, 60% and 70% flammable material and these are shown by the broken line in *Figure 1*.

Table 2
Results of Burst/Fire tests, showing number of positive results out of number of tests.

Solvent	Nominal container size	Amount of butane				
		10 g	20 g	40 g	80 g	160 g
Odourless kerosene	6 oz	4/10	10/10	8/10	0/1	—
	8 oz	0/1	10/10	9/10	9/10	—
	12 oz	1/1	10/10	10/10	10/10	8/10
	16 oz	2/2	0/1	1/1	9/10	7/10
50% w/w Water 50% w/w Methylated Spirits	6 oz	2/10	1/10	1/10	0/10	—
	8 oz	0/1	0/10	2/10	1/10	—
	12 oz	0/1	0/1	1/10	1/10	0/10
	16 oz	1/2	0/1	0/1	1/10	0/10
Water	6 oz	0/10	0/10	0/10	0/10	—
	8 oz	0/1	0/10	0/10	0/10	—
	12 oz	0/1	0/1	0/10	0/10	1/10
	16 oz	0/1	0/1	0/1	0/10	0/10

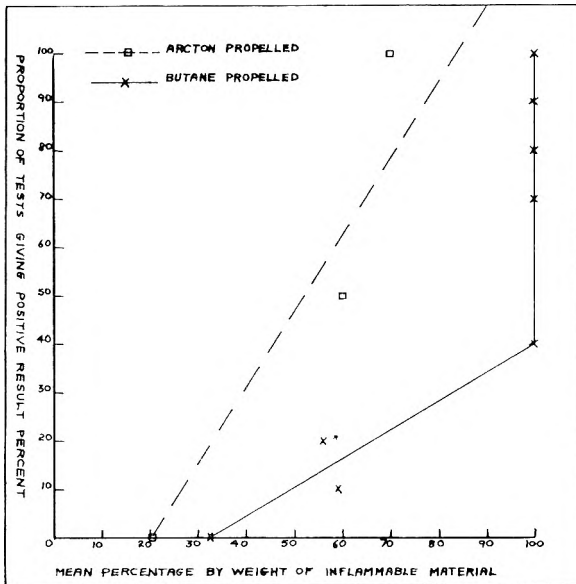


Figure 1

Graphs comparing results of Burst/Fire tests obtained from butane and Arcton-propelled pressure packs, containing various levels of flammable material.

These results suggest very strongly that the butane/water system will tolerate a greater proportion of total flammable material than will the Arcton system, if equal fire hazards are accepted when a dispenser bursts. This is presumably a manifestation of the high efficiency of a water spray as a fire suppressing, and extinguishing, medium.

FLAME PROJECTION TEST

Flame projection tests based on the C.S.M.A. Method¹ have been carried out on the spray from dispensers containing mixtures of 100/120°C petroleum ether with 50/50 Arcton 11/12 mixture, and on mixtures of commercial butane and water with emulsifiers. The filling weights and valve specification were such as might be found on production packs of this type. As there is some change in the composition of the water/butane mixture during the discharge from the dispenser, tests were performed on full packs, and those from which 50% and 90% of the contents had been discharged.

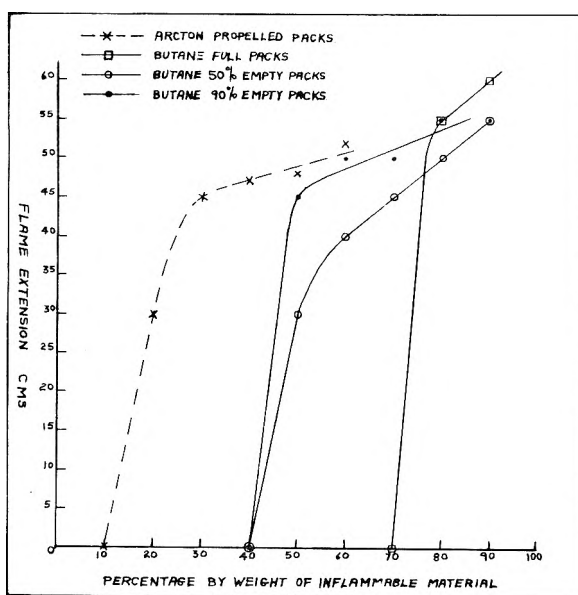


Figure 2

Graphs comparing flame extension of butane and Arcton-propelled pressure packs containing various levels of flammable material, and at different degrees of emptiness in the case of butane.

The results of these tests are plotted in Figure 2. Dispensers containing 50/50 Arcton 11/12 mixture at less than 40% w/w gave erratic results, due to poor spray characteristics and these have been omitted. The results again demonstrate the remarkable efficiency of dispersed water as a flame-suppressing medium.

COMPARISON WITH OTHER RESULTS

Kempe² has recently published a paper giving a comparison of flammability of chlorofluorohydrocarbons, vinyl chloride and *isobutane*, with a range of organic solvents and had shown that the addition of flammable solvent to flammable propellants can result in formulations which give very severe flammability risks, and the "blow torch" type of flame. It is interesting to note, however, that in all his examples both the flame extension and the flame temperature relate fairly uniformly to the total amount of flammable material present in the formulation. Thus, for example, in a system consisting of 50/50 Frigen 11/12, *isopropyl alcohol*, methylene chloride, and *isobutane*, the volume/volume concentration of Frigen is held constant while the ratio of *isopropyl alcohol* to methylene chloride in the mixture constituting the remainder of the fill is increased, giving rise to a corresponding increase in flame extension and flame temperature. On replacement of the final mixture (50% v/v Frigen, 50% v/v *isopropyl alcohol*) with 50 v/v vinyl chloride, 50% v/v methylene chloride, little change occurs in either of the measured quantities, in spite of the fact that methylene chloride, while being virtually nonflammable under normal conditions, has an auto-ignition temperature (1224°F, 662°C)³ well below the flame temperature at this stage (approx. 850°C). As Kempe points out, replacement of methylene chloride by *isopropyl alcohol* (or other flammable material) has relatively little effect on the flame temperature or extension at this stage.

Kübler, in the final article of an interesting series^{4,5,6}, gives results showing a similar pattern for a range of propellant/solvent systems.

Kübler (*loc cit*) also gives descriptions of the effects of placing dispensers filled with a range of formulations in a fire, and his findings are in general agreement with our own.

CONCLUSIONS

- (a) It is possible to make aerosol products which are completely non-flammable or intensely flammable, or anywhere in between.
- (b) While specific materials have widely differing fire promoting or fire suppressing properties, the fire hazard presented by any particular product in the hands of a consumer will depend on the balance achieved between these properties in the complete formulation. It should be noted here that formulation is not necessarily the only feature contributing to the possible fire risk, and that proper selection of other components, such as the valve, may in some instances be especially important.
- (c) Extensive experience has shown us, and other marketers of pressure

packs in this country, that packs containing up to 60% or 70% of flammable material are used safely by the general public.

- (d) The results of our own tests, and those of others, show that butane-propelled packs can be formulated to present certainly no more, and probably less, fire hazard to the consumer than is already widely accepted.
- (e) The final test on any consumer product is its performance in the hands of the user and judgement of it should be made accordingly.

ACKNOWLEDGEMENTS

I should like to acknowledge with thanks Mr. R. M. Mumford's encouragement and advice in preparing this paper, and Messrs. D. Hollinshead's and A. Glass' intrepid assistance in carrying out the experiments.

(Received: 19th February 1963)

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Introduction by the lecturer

The paper presented relates only to hazards in the users' hands, and not to any that may exist in bulk storage or transport. I do not intend to discuss this aspect, which is one where other considerations may be of importance.

My main thesis is that an aerosol pack should be considered as a whole, and that no undue attention should be paid to the inclusion or omission of any particular ingredient as such. If a pack is shown to be safe in use, then there is no point in taking exception to the inclusion of any material that may be dangerous on its own. The risk associated with a product will depend on suitable choice of materials, proper formulation and proper use of the product, as will be illustrated by three accidents which have come to my notice since my paper was written.

All concern hair sprays, one pressure packed and the others in squeeze bottles.

(1) A pressure pack was used in an American bathroom where both a gas fire and a gas water heater were going. Vapours from the spray were ignited, and the bathroom was quickly involved in flames.

(2) In this country a lady was using a hair spray packed in a squeeze bottle. It is believed that the bottle was not of a material recommended for this purpose. It split, spilling lacquer down her dress which was ignited by an electric fire.

(3) A squeeze bottle was left in front of an electric fire in a hairdresser's shop. It exploded and flashed. Some damage to the ceiling and walls of the shop occurred.

The latter two of these incidents are due to misuse of conventional products generally regarded as being safe under normal circumstances. The first savours strongly of a similar history.

No doubt many similar unfortunate incidents have occurred with other common household articles, and while appropriate precautions should be taken, and warnings given, I can see no reason for treating aerosols as a special case *per se*.

I do think, however, that appropriate tests should be applied to a pressure pack to assess the risk associated with it, and that these tests should be appropriate to the product.

DISCUSSION

MR. G. F. PHILLIPS: In connection with your flame extension experiments, using mixtures of 100/120° petroleum distillate with butane and water, (1) would you care to comment on the remarkable increase in flammability (0 to 50 cm flame extension) on progressively discharging a spray containing 70% flammable material? (2) Have you any data regarding the apparent fractionation of these formulations? (3) What significance do you attach to the crossing of the curves for full, half empty and 90% exhausted packs originally containing over 70% flammable components? The difference in flame extension at 80% is small but the three curves appear reasonably contiguous. (4) Do you consider it legitimate to classify hydrocarbon gases together with all solvents present possessing flammable vapours? Their behaviour in the emitted spray and interaction with other, non-flammable, ingredients may be quite distinct.

MR. P. DYSON: It would appear from *Figure 2* that a full container with 70% butane, 30% water and an emulsifier, with the type of valve used on this type of product (vapour phase tap, etc.) gave no flame projection. Is this in fact so? We have obtained a flame projection of 35–45 cm with such a mixture with a conventional valve, without a vapour phase tap. It is noteworthy too, that 80% butane/20% water in *Figure 2* gives a flame projection approaching 55 cm.

In my opinion the caption to *Figure 2* is most misleading. The graphs do not compare the flame extensions of butane and Arcton-propelled pressure

packs of similar types. Rather, they compare flame extension of *Arcton* propelled packs containing a highly flammable material with those of butane-propelled packs containing water.

THE LECTURER : On a point of detail in Mr. Phillips' question : I have not used 100/120 petrol with butane and water. This was used with *Arcton*-11/12 mixture, and the butane/water mixture formed a separate series of tests. However, his first point is similar to that of Mr. Dyson and serves to demonstrate the importance of correct formulation. It also demonstrates the importance of correct testing. I believe that with the mixture containing 70% butane and 30% water very rapid settling of the water in the emulsion has occurred in spite of shaking the dispenser, and most of the water was used up early in the life of the dispenser. This point should have been made explicitly in the text. Mr. Dyson's emulsions were, no doubt, more stable than those described. I believe that this also covers Mr. Phillips' second question.

I do not think that any great significance should be attached to the crossing of the curves relating to the butane packs. It is difficult to measure the flame length with accuracy, and I suspect that all are in fact converging to the same asymptote.

I cannot agree with Mr. Dyson's comment on the caption of *Figure 2*. This shows flame extensions found with two series of packs containing the same ratios of flammable and non-flammable materials. In one instance, they are *Arcton* and petroleum ether ; in the other they are water and butane. It is quite true that some of these mixtures are unlikely to be of any great commercial interest, and this applied equally to both types insofar as I am aware. If taken to the extreme one might say "because a pack contains *Arcton* it must be safe" and "because a pack contains butane it must be dangerous". Either of these bald statements is untenable, one no more so than the other.

The fallacy is, I think, in the tacit assumption that there is some magic difference between propellants and solvents, or other ingredients. I strongly suggest that the only difference between the two classes lies in their vapour pressure, and that even here the dividing line is not well defined.

This takes us to Mr. Phillips' final question. I consider it not only legitimate, but essential, to consider hydrocarbon gases together with all the other ingredients present, not only those with flammable vapours, and that the behaviour of the complete pack should be considered as a whole.

MR. A. HERZKA : Would someone care to comment on the remarks made in the paper that "leakage from pressurized packs presents no greater hazard than from other common household articles"?

MR. G. F. PHILLIPS : The lecturer quotes four (presumably U.K.) in-

idents involving aerosol containers : Explosions caused by steam, or exposure to sunlight, inversion of the base by direct heating, side-seam failure by solar heat. He refers briefly to other explosions in hotter climates. He knows of no fires primarily due to domestic use of aerosol dispensers. I find it hard to believe that there can have been only four such incidents, and one concludes that the majority of incidents have not led to serious consequences. For example, I could supply the lecturer with two more from my private experience. One, an explosion of a veterinary preparation in the storage portion of a pigeon loft left closed over a weekend. This resulted in a considerable mess and frightened the pigeons but caused no fire ; in a second incident, an aerosol container left in a closed cabinet over a hot Bank Holiday weekend, suffered inversion of the dished base sufficiently violently to damage adjacently stored glassware. This could have been more dangerous, depending on the contents of the other vessels.

But even this excellent record does not supply a premise for the lecturer's conclusion. The evidence appears to show that the containers he has considered are satisfactory ; it does *not* imply that *leakage* of the contents would present "no greater hazard than that from other common household articles". One might agree where the most hazardous component present is, say, kerosene but leakage of butane in an unventilated cupboard in which, for example, electrical switches were present, could represent a considerable hazard. It would only require the leakage of 3 oz of butane in a cupboard of dimensions 5' x 4' x 3' to furnish an explosive atmosphere (2% v/v). I therefore cannot entirely agree with the lecturer.

MR. E. EBEL : Surely the flammability of the cretonne cloth might be influenced by other factors such as the humidity of the air?

THE LECTURER : While I accept the value of flame temperature as a possible means of indicating hazard associated with flammable material, I feel that the duration of a flame is also of great importance and in the burst/fire tests the tendency has been for, what I suspect to be, the relatively low temperature flame produced by fairly heavy flammable material to be more likely to ignite the curtain, than the possibly higher temperature quick-flash obtained with some volatile materials.

MR. E. EBEL : The flash point of the formulation is a very important property. Tests using the Abel-Pensky flash point meter with subcooled (-40°C) contents of aerosols have shown that formulations with flammable propellants have flash points of the order of below -40 to -30°C . But the use of fluorinated hydrocarbon propellants raises the flash point beyond room temperature.

THE LECTURER : I agree that flash point is important, but its importance

is particularly relevant to bulk storage, which is outside the scope of my paper.

MR. E. EBEL : Why did you not compare the butane-water system with an Arcton system including some water in the solvent? From the yet unpublished parts of Kempe's investigation we have evidence that a 90% volume ethyl alcohol (10% water) shows a very remarkable reduction in the flammability hazard compared with 99.8% pure alcohol.

THE LECTURER : I did not compare the butane/water system with an Arcton system containing some water, firstly because I feel that I have compared some products or some systems, typical of those which are at present being marketed or likely to be marketed in the United Kingdom, and secondly, I felt it was interesting to compare the fire suppressant properties of water and Arcton.

MR. J. P. HALL : Do the mixtures of commercial butane with water and emulsifiers form W/O or O/W emulsions on shaking? The type of emulsion can be influenced by the ratios of the two liquid phases, as well as by the emulsifying agent. Even where a W/O emulsifying agent is used, it is possible that, at low concentrations of butane, an unstable O/W emulsion may be formed. Is this so in this work, and does it affect the results?

THE LECTURER : The mixtures which I have considered are W/O emulsions although O/W emulsions are known in aerosol packaging. We have been at some pains to see that those described in the paper did in fact have the water as the dispersed phase. I think instability of the emulsion could well affect the results obtained in flame projection tests, but is less likely to do so in the case of a Burst/Fire test.

MODERN COSMETICS—ILLUSION AND REALITY

T. J. ELLIOTT, B.Sc., Ph.D.*

A lecture delivered before the Society on 25th March 1963.

Despite improvements in modern cosmetics, many products still cause disappointment to the woman user.

Reasons for the discrepancy between advertising promise and product performance are discussed.

ALL NATURAL PHENOMENA possess a physical reality independent of the observer and an appearance or illusion which exists entirely in the mind of the observer. Reality is a primary quality and illusion is derivative; if a serious discrepancy arises between these two qualities, it is usual for the illusion to be modified to conform more closely with reality. It would be incorrect, however, to discount the importance of illusion because sometimes its power is sufficient to change reality. The French Revolution and the American Civil War were both examples of the power of ideas to effect a change in a conflicting reality.

As appearance is subjective, the same reality can present different illusions to various observers; Niagara Falls appears quite differently to a honeymoon couple, a power engineer, or an over-awed schoolboy. This contradiction does not generally present problems because most of us have grown used to the idea of living simultaneously in a real world and a make-believe world. Generally we do not bother to query this self-deception unless we become aware of a gulf between expectation and realisation—then we begin to feel cheated and dissatisfied. A simple example is the continuing sale of open cars in the United Kingdom despite the well-known characteristics of English weather. The illusion of driving along in glorious sunshine persists in face of all experience to the contrary. But it is imperative that the open car should have a rain- and draught-proof hood, otherwise the illusion would collapse in the face of the wet and cold.

In the same way, a woman who buys a cosmetic is deceived because the product is invested with subjective attributes based on her desire to be more beautiful. She is a willing agent in self-deception and will only protest if the deceit is too blatant. If women were allowed to create their own illusions regarding cosmetics, perhaps the gap between illusion and reality would not be so great but modern selling methods rely on creating ready-made illusions for the customers.

*Innoxia (England) Ltd., London, N.1.

This places cosmetic chemists in a difficult position as they become increasingly aware of the widening gap between their products and copy-writers' prose. In the process of making products designed to satisfy the innate desire of women for the beautiful and unattainable, they must learn to work with those who are responsible for creating the illusions. Similarly, the advertisement and sales men must realise that behind their flowing prose and elegant packs is a product which will ultimately be used by the purchaser, a regrettable necessity which should compel them to recognize the importance of technically competent products!

In the cosmetic industry the illusions created are so attractive and powerful that unless the products are more than averagely competent, a large number of users will experience disappointment. Unfortunately, the comparative ease of selling cosmetics on illusory merits could lead to a state of comparative technical backwardness in the industry.

Leaving aside specialized work on the skin, which is mainly carried out elsewhere, it would be fair to state that most of the activities of cosmetic chemists are directed towards the production of better cosmetics. But the concept of "better cosmetics" can include a whole number of improvements in product stability and shelf life which do nothing to improve their actual application and the appearance on the skin. For example, present-day cosmetic creams seldom exhibit symptoms of emulsion break-down or develop gross bacterial contamination. Cosmetics and toiletries no longer corrode the collapsible tubes in which they are packed. Lipsticks do not develop rancidity and symptoms of pigment separation in the crayon. These improvements are only designed to enable the product to reach the customer in a better condition, which comes within the designation of shelf testing rather than user testing. Whilst we can be fairly confident of the thoroughness of shelf testing the situation with regard to user testing is much less satisfactory.

Once a woman commences to use a product, she is evaluating the illusion-reality relationship. The discrepancy she finds between these two qualities will influence her decision to repeat her purchase or throw the product away in disgust. Our ability to discover from customer complaints the seriousness of this discrepancy is limited. It would be much better to evaluate the special features of the relationship for this particular product in advance and to conduct adequate user-testing to ensure that the discrepancies are not abnormal.

The gap between illusion and reality is not constant over the whole range of cosmetic products and it is now proposed to examine this variation in greater detail. It is possible to divide cosmetics into three main groups—skin care, make-up and specialities. As a broad generalisation, the discrepancy may be said to vary with the group, being greatest with skin care

and least with the specialities, make-up standing half-way. The differences are partly basic to the group, e.g. it is much more difficult to demonstrate the effectiveness of a cream which will moisturise in "x" minutes, than a depilatory which removes hair in "x" minutes. There are, however, other factors which reflect the failure of the technical side of the industry to provide the best possible products within the limitations of a particular group.

Cosmetic specialities are many and varied; representative examples include anti-perspirants and deodorants, depilatories, suntan preparations, shampoos, hair lacquers and hair waving preparations. With most of these products, women find what they have been encouraged to expect from the advertising and sales promotion. This is often restrained, sometimes informative and occasionally cautionary of the results which can be expected. The reason for this modesty is due to the fact that it is possible for the user to make critical comparisons of both the product and promise and, even more important, of various brands of the same product. Even the most sophisticated advertising will not persuade a woman of the speed and safety of a particular depilatory if it takes 15 minutes to act and leaves her skin raw and inflamed. With suntan preparations, anti-perspirants and home perms, the ability of the user to make objective comparisons between the various brands has the interesting result that the selling value of an expensive name is at a discount and these particular products are brought largely on their merit. Much technical effort had to be put into the formulation of these products to enable them to withstand this user appraisal. Thus, the comparatively low key to which the users' expectations are pitched, together with the existence of a basis for real criticism of the products, makes it difficult to sell inferior products however well they may be advertised.

This group of products is generally satisfactory not because it presents easier problems of formulation than the other two groups, but possibly because testing is easier. Few scientists would quarrel with the proposition that formulation and testing should be a continuous process in which changes of formula are immediately evaluated and the final test on the final formula merely a confirmation of all the work which has gone before. The testing of cosmetic products, by which I mean solely their evaluation by users or potential users, is still at a rudimentary stage, and conventional laboratory testing is only of limited help.

It is fortunate that in the specialities group, the product characteristics which enable the user to differentiate between good and bad products also enable semi-quantitative laboratory tests to be developed which are of enormous value in formulation. For example, the successful depilatory is a compromise between speed of action of hair removal and potential skin damage. Variations in ease of hair removal between individual testers can

often be greater than those produced by formula changes, so that there is a need to carry out experiments on uniform switches of hair. In this way speed of action can be evaluated by studying the factors which are likely to influence it, e.g. pH, strength and type of active agent, effect of different cations, etc. Testing on human subjects to determine the irritation factor should then result in a practical depilatory. Similarly, shampoo formulation and testing can be carried out using switches of hair under conditions which approximate closely to the salon, and measurements made which would be difficult to carry out in the salon itself. Anti-perspirant and deodorant products would certainly not be as effective as they are today if the only methods of assessment were subjective, but in fact the amount of perspiration secreted in a given time can be determined, whilst bacteriological tests give a good index of deodorant effectiveness. Many more such tests have been developed along the lines of those described as useful aids to formulation. On this basis, formulation and testing can proceed simultaneously and for the development of this group of cosmetics the laboratory does not need to be organised in a different way from other laboratories in the field of applied chemistry, e.g. paint or textiles laboratories.

The potential user is keyed to a higher degree of expectation with make-up preparations than with the specialities group, and the discrepancy between expectation and performance is greater. Beautiful models, presented with all the skill of modern advertising, create an illusion which is certainly not within the capabilities of the average woman to attain. It is, however, reasonable for the average woman to assume that if these products create an illusion of outstanding beauty on models she will also appear more beautiful when she uses them.

Until a few years ago, perhaps it would have been justified to claim that the current lipsticks were just about as good as they could be—but not today. The darker shades with which we were then satisfied are rapidly disappearing from the market and in their place are clear, bright, pastel shades. No doubt the glowing prose describing these lipstick colours *in the crayon* is fully justified; they are clear, bright, subtle, sunlit and basically there is no conflict between reality and prose. But lipsticks are ultimately worn and judged on the lips, even if they are bought on crayon colour and rub-out colour on the wrist. Modern lipsticks exhibit certain defects primarily caused by the need to incorporate increased amounts of titanium dioxide to obtain paler shades. The emergence of eye make-up has compelled women to use subdued pastel lipstick colours to avoid a major clash of interest on the face and as the use of eye make-up is likely to increase considerably, this factor alone makes the return of dark lipstick shades unlikely.

Orange, coral, peach and pink lipsticks exhibit the true crayon colour

for a comparatively short time on the lips and then a number of changes take place which seriously impair the appearance. Reflocculation of the white titanium dioxide occurs mostly in the crevices of the lips, emphasizing all the contour defects of the lips instead of helping to conceal them. With orange and peach lipsticks, this is often accompanied by a break up of colour into a mosaic of individual pigment colours, usually during eating or drinking. Finally, due to the incorporation of too high levels of the wrong coloured stain, the residual colour on the lips may bear no resemblance to the original crayon colour, e.g. orange and peach lipstick turning pink, and brown lipsticks turning red. There are one or two ways of evading this problem, such as drastically reducing the pigment level, which makes the pigment flocculation less noticeable, but such a lipstick is so lacking in covering power as to be quite unfashionable.

Most women feel strongly on the subject of these defects and it is no consolation to be told that only the paler shades exhibit these faults when it is precisely these shades they wish to wear. Insufficient attention is being paid by chemists to a problem which, in masculine eyes, is more aesthetic than technical. For example, flotation of titanium dioxide in lipstick manufacture causing streaking in the crayon was considered a serious technical defect and has now been overcome, but the reflocculation of the same pigment on the lips is an even greater defect in the eyes of the user.

Until recently eye cosmetics were even less satisfactory than modern pastel lipsticks. In the past, mascara, eye shadow and eye liner probably caused more disappointment than any other coloured make-up items. It would be reasonable to assume that the present increased use of eye cosmetics is partly due to their better performance and they may now be worn during the daytime with more confidence in the durability of the colour effect. In particular, the development of waterproof mascara in either cream or roll-on form has eliminated the main bugbear of streaking which was associated with the earlier block mascara. An additional advantage of waterproof mascara is the reduced likelihood of eye irritation due to the absence of soap, although the choice of unsuitable solvents in some waterproof mascara formulae does cause a very uncomfortable feeling on the eye-ball owing to solvent evaporation.

With eye shadow, the present position is not particularly satisfactory, although it is likely that this will be radically transformed in the near future. Instead of the delicate graded wing of colour implied by the advertisements, reality has been a very fugitive approximation to this illusion, to be followed by the development of ugly coloured lines in the eye area and the complete loss of overall colour. All eye shadows which contain substantial quantities of waxes or oils, in cream or stick form, must inevitably run into coloured lines; the policy of powdering over only delays the inevitable—it never prevents it. Whilst attempts have been made to formulate non-greasy eye

shadows, conventional eye shadows still outnumber the new types by at least five to one in terms of brands available. Whatever the defects of these new eye shadows, it is worth concentrating on their solution rather than continuing to produce the defective greasy eye shadows.

The most dismal approximation of reality to illusion is to be found in liquid eye liner, so dismal in fact that many women have reverted to pencils, block mascaras or even foundation make-up in an attempt to provide a more satisfactory way of drawing a line on the eyelid. From experiences in the paint industry, and from nail enamels in our own field, the selection of a correct viscosity of fluid for brush application ought to have been assured. But whereas viscosities of most nail enamels are in the region of 300 to 400 centipoises, the viscosities of eye liners range from below 100 centipoises to over 50,000 centipoises. Moreover, wide variations in viscosity are not only encountered between one brand of eye liner and another, but often between different shades of the same brand. Drawing a well-defined line on the eyelid with a brush is not an easy task, and if there are wide variations in product consistency, it is virtually impossible. Too thin a liner will run down the lashes and leave smudgy edges, whereas the very thick liners will not flow out evenly to give a smooth finish. Furthermore, the high alcohol levels characteristic of some eye liners, not only produce the rapid drying desired, but owing to the high solvent phase volume result in considerable shrinkage of the final film on the lids; this gives an uncomfortable feeling, often described by women as "sewn up eye lids". Finally, and most serious of defects, eye liners lack the necessary flexibility and adhesion to survive the estimated 40,000 blinks of the eyelid in the course of the normal wearing time. It is not uncommon for the film to break up into a mosaic of cracks or even for whole sections of the line to flake off; but it should not be necessary for a woman to carry around a bottle of eye liner and a brush for touch-up purposes.

Other make-up items could be examined in a similar manner, e.g. face powders which change shade on the skin and rouges which are difficult to shade off; these also tend to display basic technical defects. It is therefore necessary to seek an explanation for the fact that make-up preparations are generally less satisfactory than specialities, assuming that it is basically no more difficult to make good lipsticks or eye cosmetics than to make good depilatories or hair lacquers. One of the possible reasons is that technical specialists tend to attach too little importance to the aesthetic aspects of their products. With few exceptions they are not involved in actually using coloured make-up and the irritation felt by the user of a "bitty" lipstick, running eye shadow or flaking eye liner is not directly experienced. There appears to be a similar lack of appreciation of the aesthetic importance of colour-true, stable make-up. The lipstick crayon, the eye shadow stick and

the pot of eye shadow are often ends in themselves, to be judged solely in comparison with other crayons, sticks and pots, whereas the real end-point is the creation of more attractive women. To quote a well known writer : "Too many scientists are interested in colour photography and Hi-fi rather than in art and music".

Another important factor is the problem of devising satisfactory development and formulation testing for these products. Unfortunately, make-up does not lend itself to the laboratory test procedures developed for specialities, and the only meaningful test is application on the face. Most of the standard test procedures used in the cosmetic industry for the consumer evaluation of products have serious limitations, especially when used for testing make-up items and better tests will certainly have to be devised. Best known is the comparatively large representative panel of women chosen, for example, by the advertising or market research agency. This type of panel is anonymous as far as the laboratory is concerned and can only be used for the testing of final or near-final formulations, through the medium of replies to a standard questionnaire. By its very nature, this will only discriminate between gross differences in products and its only real value is to confirm an answer which is already known.

Most cosmetic houses also test products through their own beauty salons which appears to be an obvious and helpful procedure, but since the products will obviously be linked with the house name, only testing of the near-final formulations is possible. Even in this respect, the tests can be quite misleading as both users and method of use are untypical with respect to the main sales market. Application of the products is carried out by beauticians whose skill and experience will overcome most defects of the product whilst the clientele of the salon will, in general, consist of women in the older age group whose opinions on colour, texture, etc., will often be quite different from the average. A more useful panel may be set up inside the cosmetic house, consisting of factory and office personnel in the proportions which more or less constitute the market of the particular house. There are difficulties in having such a panel under direct laboratory control, the most important being the natural reluctance of heads of departments to allow time off for staff during the day to test cosmetics under laboratory supervision. As a result the cosmetics are usually tested at home.

The main criticism of all these types of test procedures is that the testing of the products is either partly or wholly divorced from the laboratory. The type of test procedure which is most fruitful for the development of better cosmetics is one in which highly trained and experienced girls take the place of laboratory apparatus. The panel should preferably be small in number so that it can function easily as part of the laboratory service and the cosmetic likes and dislikes of each panellist are well known. For example,

the durability and attractiveness of lipstick, nail enamel and eye make-up are all strongly dependent on the subjective attitude of the particular user to the shade worn and it is important to be aware of this. As this is a professional panel and will spend most of its time testing either one's own or competitive products, its members will develop good critical faculties. Products can be tested in the early stages of formulation, and unsatisfactory products eliminated, for the chemists will hardly be able to escape criticism at such close quarters. This type of test procedure has little in common with the use of women members of the laboratory staff on a haphazard and occasional basis of product testing.

In the field of skin care products, such as the moisturising creams and lotions, night creams of all types and the so-called medico-cosmetics, there is an unbridgeable gap between the illusion of eternal youth and the hard reality of advancing age—a gap which cannot be closed by any cream. Scientists tend to regard with much cynicism the extravagant claims made by copywriters. In addition, certain well meaning champions of the public good seize upon these particular cosmetics to paint the picture of an unscrupulous industry selling worthless products at high prices to foolish, gullible women. The nett result of these factors could be the production of a negative attitude to the formulation of better skin care products.

The outlook for altering the appearance of the skin by the use of medico-cosmetics is not encouraging. The use of therapeutic substances, as in the pharmaceutical industry, to produce definite changes in or on the body may produce undesirable side-effects. The risk involved has to be calculated and, as recent history has shown, can be tragically wrong. There may be some justification for this risk in the pharmaceutical industry, but none whatever in the cosmetic industry. For this reason, the incorporation of therapeutic substances into cosmetics must be carried out in such a way that no one can possibly be harmed, either because of undue sensitivity or through prolonged use or mis-use. This imposes limitations on the type and dosage level of therapeutic substances available for incorporation into medico-cosmetics. Even when an active ingredient is discovered which produces visible changes on the skin, the permissible dosage and potency of the agent will be at such a low level that only a small minority of women are likely to experience any real benefit. Fortunately, this apparent deadlock does not mean the prohibition of legitimate skin care products.

To return once more to the pharmaceutical industry, a substantial number of products of no proven value are prescribed by doctors and used by grateful patients; this includes, for example, "tonics", sedatives and tranquillisers. Just as women seek eternal youth, knowing that it cannot be achieved, so do many people seek tranquillity in a tablet, knowing that the real problem is the life they live. The desire to have some actual product

for illnesses which are either fanciful or the cure of which will never be found in a tablet, is so strong that no doctor could refuse to prescribe. Similarly, the desire of women to stay young in appearance needs creams and lotions to reinforce and encourage the illusion. On this basis, the average skin care cream is just as necessary and no more fraudulent than the well known compound of glycerophosphates "tonic". Although there is no cream which will arrest the appearance of age or turn the clock back, there is evidence to support the theory that women who have regularly used skin care preparations have better skins than those who have not.

Expensive packaging will convey to the user the idea that a product is considered worthy of a luxury pack, whereas a cheap pack can only reinforce her own doubts about the value of all such products. Additionally, as the putting on and cleaning off of night creams over a period of ten or twenty years can become rather boring, a package and product is required which will convey a certain sense of uniqueness and pleasure. Measured in this way, some of the skin care products on the market are either well below the standard required or possibly formulated to another conception altogether. For example, one could formulate skin care products along so called "medical" lines, on the basis that all "do you good" preparations are more or less unpleasant. This might account for the continued existence of the traditional greasy, heavy night cream in which the perfume has utterly failed to cover the basic unpleasant odour of the fats and other ingredients. The pharmaceutical industry, however, has moved completely away from this concept of medical preparations in the last decade and development work has been carried out to make medicaments more acceptable to the user, for there is more likelihood of the patient continuing the dosage if the medicine is not unpleasant to take.

In persuading women to use skin care preparations as early as possible in life and to continue with their use, it is equally necessary to develop products which are not repugnant either to the user or to any other person in the vicinity. The oily, unaesthetic night cream has no more place in the present-day bedroom than the wearing of curlers or the habit of taking out one's dentures overnight.

Elegance and pleasure must also be strongly associated with the product and pack of the moisturising or day creams and lotions. It must be distressing to purchase a moisturising cream named "Heavenly Petal Dew" only to find that it will not pour readily out of its bottle, or that, in the case of a polythene pack, all that is left of the perfume is a strong candle-like odour.

The cosmetic industry today is expanding at a rate well in excess of the average increase for industry generally. From this, one can only conclude that not only are more women buying cosmetics but that all women are

buying more cosmetics. This points to the cosmetics market becoming a mass market in the same way as the toiletries market. As the mass market is much more ruthless in dealing with over-priced, inferior products than the luxury market, now is the time to eradicate such products. Their existence can only serve to hold back the development of the mass market because an unsatisfied user can easily become a non-user.

Those of us who are on the technical side of the industry should be the severest critics of its products.

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THE ANALYSIS OF SYNTHETIC DETERGENTS

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A lecture delivered before the Society on 15th May 1963.

The subject is introduced with a classification of surface active agents that are used in all types of detergents. This is followed by a review of the older qualitative tests and then an outline of a new paper chromatographic procedure. Quantitative analysis, confined to the determination of the active constituents, is described under headings of solvent extraction, colorimetric determination, anionic-cationic titration, and miscellaneous methods.

THE WORD detergent nowadays suggests the packet of spray-dried powder used for domestic washing purposes, but liquid products used in the same field may also come to mind. For the purposes of this paper other cleansing materials, namely shampoos and toothpastes, will be regarded as detergents; soap is excluded as not falling within the definition of synthetic. However, only the organic surface active ingredients of the detergents will be considered.

Most surface active agents which are used as detergents have molecules which are essentially linear and contain at one end groups having an affinity for water (hydrophilic groups), and at the other end groups which are anti-pathic to water (hydrophobic groups). Surface active agents are classed according to whether the active species is an anion, a cation, a non-ionizing group or an ampholytic group. An ampholytic group is one which may act as either anionic or cationic depending on the circumstances, principally on the pH value of the solution. Hydrophobic groups may be classed under the headings of carboxylic acids (mainly naturally occurring acids), alcohols, hydrocarbons (mainly synthetic hydrocarbons derived from petroleum), and others (polyoxy propylene chains). Between the hydrophilic and the hydrophobic group, the molecule may contain a linking group which may be an ether, ester, or amide. The listing and classification of possible structural groups is an essential prerequisite to the construction of a scheme of qualitative analysis, and we still find the classification¹ drawn up five years ago to be a useful starting point. The best systematic procedure is to identify first the hydrophilic group, then the linking group, if any, and lastly the hydrophobic group.

QUALITATIVE ANALYSIS

Hydrophilic groups

One of the best tests for anionic and cationic active compounds is to

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treat the substance with a coloured reagent of the opposite ionogenic type and shake the aqueous mixture with a non-polar liquid such as chloroform. The reagent should be such that its salts with inorganic ions are not extracted by the solvent, but its salts with surface active agents, containing a hydrophobic group in each molecule, will be readily extracted; the appearance of the coloured molecule in the organic layer will show the presence of a surface active agent.

The usual reagent for anionic surfactants is methylene blue, but this can be used only in acid solution and cannot therefore detect the carboxylate group. Dimidium bromide² can be used over a wide range of pH values and can therefore be used for carboxylate groups as well as sulphate and sulphonate. For cationic surfactants, a wide range of dyes and indicators containing the sulphonate group is available and bromophenol blue seems to be most commonly used.

An alternative procedure for detecting anionic or cationic surfactants is to test whether the substance will discharge the colour produced with a known surfactant of opposite type and an appropriate reagent. To test for an anionic surfactant, an aqueous alkaline solution of bromophenol blue plus a trace of a cationic surfactant is shaken with chloroform, and then the sample is added and the mixture again shaken. To test for a cationic surfactant, the material is added to acid methylene blue plus a trace of dodecylbenzene sulphonate plus chloroform. A compound which discharges the colour of the chloroform layers in both anionic and cationic tests is an ampholytic surfactant.

Most non-ionic detergents are of the polyethanoxy type and these will combine with large anions, such as ferrocyanide, cobalthiocyanate, molybdophosphate, giving precipitates with the cations present, barium being needed in the case of the last. Another test for ethanoxy groups is due to Rosen³ and consists of heating with phosphoric acid and testing for acetaldehyde. The polyhydric alcohol type of non-ionic surfactant also reacts with large anions; complex iodides are often used, but hexanitratocerate is a simpler though less specific reagent.

Linking groups

The linking group is best investigated by studying the stability of the molecule towards acid and alkaline hydrolysis. In the case of an anionic surfactant, aliquot parts of a solution are assayed by a colorimetric or titrimetric method (a) without hydrolysis, (b) after refluxing in N alkali for 30 minutes, and (c) after refluxing in 2N sulphuric or hydrochloric acid for 2 hours. The sulphate group itself is essentially stable to alkali and is hydrolyzed in acid solution, esters are completely hydrolyzed in both acid and alkaline solutions, while amides are partly hydrolyzed in both media,

the extent being characteristic of the particular amide. If the sample is a sulphate, or is a non-ionic compound, then more specific tests for the ester and amide links are needed. The hydroxamic test for esters is very useful⁴, while amides can be detected through the primary or secondary amine produced on hydrolysis.

Hydrophobic groups

The hydrophobic groups are examined after hydrolysis of the surfactant : mild alkaline hydrolysis is sufficient for carboxylic esters, moderate acid hydrolysis for sulphates without a linking group, prolonged acid hydrolysis for amides, hydrolysis with hydriodic or hydrobromic acid for ethers, and hydrolysis with concentrated phosphoric acid for sulphonates without a linking group. The liberated acid or alcohol may be analyzed for acid value or hydroxyl value, but a much more useful technique is gas chromatography, which is applicable to hydrocarbons also. Aromatic rings and ethylene bonds may be detected without hydrolysis; ultra-violet spectroscopy is most useful for the former whilst other physical methods such as infra-red spectrophotometry and mass spectra analysis may also be used.

PAPER CHROMATOGRAPHY

This technique is one of qualitative analysis, but it is usefully discussed under a separate heading. Over the past few years we have developed a comprehensive scheme of identification of detergent components using paper chromatography. Toluene and xylene sulphonates, urea, and alkanolamines or metals used for neutralization are tested for in addition to the main surfactants which are examined in respect of their hydrophilic groups, linking groups and hydrophobic groups. Full details have recently been given by Drewry⁵ and, therefore, the present paper will be restricted to a brief outline of the scheme and an account of the developments that have been made since the former paper was written.

Paper chromatography is essentially a separation by partition between the stationary water and moving organic solvents, and the first requirement is an optimum initial water content of the paper. In our laboratory it has been found that washing the paper (Whatman No. 1) in 50% ethanol, and allowing it to dry in the air is sufficient. In other laboratories it may be necessary to experiment with different drying conditions.

Initially, a large number of solvents was tried, but a mixture based on tertiary butanol was the only one that gave a uniform development in the presence of surface active components. Later it was found that an ethyl acetate mixture as described by Gasparič *et al*⁶ gave equivalent results to the butanol solvent, though in a development time of only 2-3 hours instead of 15-20 hours. The solvent also contains a little ammonia and methanol.

It deteriorates after a few days, possibly because of reaction between the ester and ammonia. Upward development of the chromatogram is the preferred technique because of its simplicity.

Pinacryptol yellow is a very useful reagent for detecting the surface-active agents in the chromatogram, giving under ultra violet illumination an orange fluorescence with most anionic surfactants, and blue with cationics. Amine oxides and non-ionics surfactants, of higher R_F values, also give blue colours with pinacryptol yellow, and toluene and xylene sulphonates, of lower R_F values, give orange colours. Characteristic changes occur in the spots on heating, and a subsequent spraying with Rhodamine B also modifies their appearance and makes many spots more definite.

Exposure of the paper to iodine vapour gives dark brown spots with ethylene oxide derivatives, amine oxides and cationic surfactants. It also gives spots with alkanolamides, alkanolamines, and metals, but these disappear in a few minutes. Spraying the paper next with bromocresol green solution shows all alkaline regions due to the amine oxides and cationic surfactants already detected, to the various alkanolamines which can then be identified from their various R_F values, and to alkali metals which remain at the origin. The metals can subsequently be separated on another chromatogram with a more mobile solvent of methanol and ammonia solution (9+1). A spray with cobalt thiocyanate is useful for confirming the presence of ethylene oxide derivatives and amines that were revealed by the iodine treatment, and a spray with dimethylaminobenzaldehyde is used to test for urea.

During the last few months the ninhydrin tests for amines has been found useful. Purple spots are developed after heating to 80°C with primary amines or 120°C for secondary and tertiary amines. These confirm the presence of the alkanolamines detected with bromocresol green, but also indicate the presence of mono- and diethanolamides in spots near the solvent front. It is suspected that these spots are due not to the substituted amides as such but to amine-ester impurities. The ninhydrin reagent is also sufficiently sensitive to detect the traces of free alkanolamine present in the alkanolamides added in the manufacture of the detergent. The ninhydrin spray may be followed by acetaldehyde and nitroprusside which gives a useful distinction between primary amines (khaki spots on clear paper, not readily visible after ninhydrin) and secondary amines (deep blue spots). Drewry described the successive application of all spray solutions to the same chromatogram, but the incorporation of ninhydrin into the list of treatments tends to overwhelm the paper and it is best to develop two chromatograms and apply the first five sprays to one series and the last two to a duplicated series of spots. Another small change

made from the published procedure is the rather obvious simplification of using one marker solution containing all the reference compounds.

Another method of identifying amides, applicable both to the nonionic alkanolamides used as additives and to amide sulphonates and carboxylates used as the main anionic surfactants, is to apply paper chromatography after acid hydrolysis. The aldehyde nitroprusside spray is the most useful as it distinguishes primary amines such as monoethanolamine and taurine (khaki spots) from secondary amines such as diethanolamine, N-methyltaurine and sarcosine (blue spots), all liberated by hydrolysis of the corresponding fatty acid amide.

QUANTITATIVE ANALYSIS BY SOLVENT EXTRACTIONS

The most reliable technique of analysing mixtures of surfactants is a series of extractions, with solvents and ion-exchange resins, before and after hydrolysis, to separate the individual fractions which are then weighed. Each fraction can, if desired, be characterized by further analysis including physical methods such as gas chromatography. A series of separations can be assembled in a variety of ways and therefore it seems best here to discuss the subject under sub-headings of the solvents. The general method for liquid-liquid extractions is to use stoppered separating funnels, and for liquid-solid extractions is simple stirring in a beaker or centrifuge tube, followed by filtration or centrifuging.

Light petroleum

Typical procedures for petroleum extraction are described in the B.P. and U.S.P. monographs for sodium lauryl sulphate. The sample is dissolved in 50% ethanol, for the unsulphated alcohol is less soluble in this than in an aqueous solution of the sample (owing to reduced micellar effects) and emulsification difficulties are fewer. Three extractions with petroleum are made. The combined extracts are dried, the solvent is distilled off and the residue is weighed. A certain proportion of free lauryl alcohol remains solubilized in the surfactant solution, as is shown by tests on synthetic mixtures, even after 5 or 10 extractions. The loss depends on the concentration of surfactants and, for reproducible results, the latter is arbitrarily fixed at about 5% w/v. Besides the question of completeness of extraction there are several other difficulties in arriving at a standard method of high reproducibility. Washing the petroleum extracts is always liable to cause losses, and these must be balanced against the errors due to contaminants. Drying the extracts with sodium sulphate or another desiccant may lead to a loss, but omission of the drying step may cause losses by volatilisation in steam. Removal of the solvent without loss of volatile alcohol is also a problem and, finally, errors associated with weighing the residue in a large

glass flask, namely, adsorption of moisture on the glass, electrostatic charges, and buoyancy errors, can all be significant.

Other uses of light petroleum as an extractant are to separate unsulphonated oil from alkylarylsulphonates, and to extract fatty acids liberated by acidification of soap solutions. The solvent is also used to extract acids and alcohols liberated by the hydrolysis of amides and esters⁷.

Ethyl ether

Ethyl ether extracts the same compounds as light petroleum, and several others too, particularly alkanolamides. Being a single compound of low boiling point it can be distilled from the extract with less uncertainty than attends the removal of light petroleum, and for this reason it is preferred in such determinations as the total fatty alcohol in alkyl sulphates. Disadvantages of ethyl ether are its higher solubility for water and for hydrochloric acid. It can only be used with dilute aqueous ethanolic solutions and is therefore not very satisfactory for extracting alcohols and acids from solutions of sulphonates as a moderate ethanol content is needed to reduce micellar effects. Ethyl ether will extract hydroxy-acids which light petroleum will not.

Ethyl ether will also extract alkylarylsulphonic acids from 2N hydrochloric acid, and this is useful for separating these acids from toluene- and xylene sulphonates⁸.

Accurate quantitative determinations are limited by the same factors as described for light petroleum, and these also apply in varying degree to the other solvents below.

Chloroform

This solvent will extract most ethylene oxide derivatives, including those with chains of six or more units which are not extracted with ethyl ether. It will also extract alkylarylsulphonates, and many other surfactants, from neutral solutions. One disadvantage of chloroform is that any ethanol in the aqueous solution must first be expelled, and even in the absence of ethanol, emulsification is often troublesome.

Alcohol

Extraction with ethanol is used to determine the total organic content of built detergents, and by separately determining unsulphonated matter, additive, chloride, etc. the surfactant content can be found. To ensure extraction of small quantities of active material contained within the beads of spray-dried powders, it is necessary to take the residue after a few extractions, dissolve it in a small quantity of water, and reprecipitate with alcohol. As ethanol is miscible with water it is clear that extraction from a solid

is the only suitable technique. However, butanol and higher molecular weight alcohols are immiscible with water, while isopropanol is immiscible with a concentrated aqueous solution of sodium carbonate, and these can be used in liquid-liquid extractions.

Ion-exchange resins

The use of ion-exchange resins differs from the solvent extraction techniques, but it is usefully considered with them as, along with extractions, it can be built into a composite analytical scheme of separations. Ion-exchange resins provide the only simple means of separating anionic, cationic, and non-ionic surfactants. Though simple in principle, the practical use of ion-exchange resins with surface-active solutions involves several complicating factors such as the polarity of the solvent, usually an aqueous alcoholic medium, the swelling and shrinking of the resin, and hydrolysis of the surfactant on the resin or during elution. A great deal of work on the subject has been done by P. Voogt, among others, but only a little of this has yet been published^{9,10}.

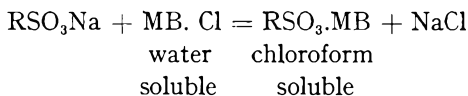
Comprehensive scheme of analysis

The number of combinations of different surfactants that may be present in a commercial detergent is infinite, and no efficient general scheme of separation can be drawn up; the method of analysis must be chosen to deal with the particular types of ingredient known or expected to be present. One decision to be made in dealing with several components is whether to extract them one at a time by the successive application of specific techniques or whether to proceed by division and sub-division, e.g. with six components, first separate two or three from the others, then proceed separately with each group. The latter technique is more complicated, but errors are smaller. Another decision is whether to separate each component in a reasonably pure form, or whether to extract two more more ingredients together and deduce the contents by difference. The case of a simple detergent containing free oil, ethanolamide, and alkylarylsulphonate, together with inorganic salts and water may be taken as an example. *Scheme 1* is to extract the free oil with light petroleum from a 50% aqueous ethanolic solution of the sample, then the alkanolamide with ethyl ether after dilution to 20–30% ethanol, and finally the alkylarylsulphonate with chloroform from the residual aqueous solution, or with ethanol from a dried residue. *Scheme 2* is to extract the first two components together, using ethyl ether, then separate these later and to extract the alkylarylsulphonate from the aqueous layer. *Scheme 3* involves extraction of free oil with light petroleum, free oil plus alkanolamide with ethyl ether, and the total of the organic compounds with ethanol, all on separate samples and the individual

contents is deduced by difference. In a simple case such as the above, the respective merits of the different approaches are readily ascertained, but with more complex mixtures, especially those containing ethylene oxide derivatives, a great deal of work is needed to find the best scheme of separation or even to find a good one.

COLORIMETRIC DETERMINATION

Colorimetric methods of determination are not used so much as volumetric, but they are better discussed first because they employ reagents which are used as indicators in volumetric procedures. The most widely used colorimetric method for anionic surfactants is that of Jones¹¹ which consists of shaking an aqueous solution of the sample with methylene blue (designated MB. Cl) and chloroform. The surface-active agent forms a salt which is chloroform-soluble, while the excess of methylene blue remains in the aqueous layer, e.g.



By spectrophotometric measurement of the blue chloroform extract, or by comparison with standards, the surfactant content of the solution can be determined. Subsequent workers have tried to eliminate interferences to which the method is subject, and a useful procedure for analysing river water and sewage effluents is that of Longwell and Maniece in which a preliminary extraction with methylene blue from alkaline solution is carried out. Methylene blue is readily oxidized to azures which may be present in the reagent when purchased and which interfere with the colorimetric determination as they compete with methylene blue for the anionic surfactant. The azures can be readily removed by a pre-extraction as described by Abbott¹². Some of the triphenylmethane dyes, such as rosaniline, have also been used, but we have found them to be much inferior to methylene blue.

Carboxylic acids are surface active only in neutral or alkaline solution, and methylene blue cannot be used for their determination. The only suitable alternative reagent, discovered after a wide search, is dimidium bromide, described by Holness and Stone². For cationic surfactants, a wide range of reagents is available; bromophenol blue is frequently used, though we have found methyl orange¹³ to be better, as it can be used at lower pH values giving more precise results with primary, secondary and tertiary, besides the quaternary amines.

For determining non-ionic surfactants, most colorimetric methods are based on precipitation procedures and use a conventional colorimetric or titrimetric estimation of the inorganic reagent in the precipitate or filtrate.

Colorimetric procedures that do not require a separation by filtration or centrifuging are adaptations of colorimetric tests, a starch-iodine procedure and a cobalt thiocyanate method having been published.

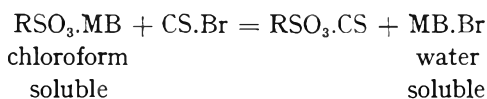
THE ANIONIC-CATIONIC TITRATION

Anionic and cationic surfactants, when present together in aqueous solutions, will neutralise the surface-activity of each other. This is the basis of an early technique of anionic-cationic titration in which one species is determined by titrating with a standard solution of a surfactant of opposite type, neutralisation of surface-activity being shown by a sharp rise in surface tension. Another means of end-point detection was based on the colour change of an indicator in the presence of long-chain quaternary compounds, and the change of bromophenol blue from purple to sky-blue was used by Hartley and Runnicles.

End-point detection

A more precise procedure was devised by Epton, and by Barr, Oliver, and Stubbins. They introduced an organic solvent to extract the salt of the indicator with the excess of surfactant of opposite type, and the end-point was denoted by the movement of an indicator ion from one phase to the other.

If a cationic indicator such as methylene blue is used in the titration of an anionic surfactant, it first forms a chloroform-soluble salt according to the equation of the previous section. During titration with a cationic surfactant, the free anionic compound, that is to say the acid or sodium salt, reacts first and then the methylene blue salt begins to react causing the indicator to return to the aqueous phase.



The end-point may arbitrarily be taken as (a) the first appearance of blue colour in the aqueous layer, (b) the complete transfer of blue colour to the aqueous layer, or (c) partial transfer to the appearance of equal colour intensities of the two layers.

The titration may also be done in the reverse manner, adding the indicator to the cationic surfactant in the titration vessel and titrating with an anionic surfactant. The choice of end points is among (d) the first appearance of blue colour in the chloroform layer, (e) the complete transfer of colour and (f) partial transfer to the chloroform layer to give equal colour intensities of the two layers.

Cullum's paper¹⁴ pointing out the existence of equilibria at the end-point

is important and shows the reasons why end-points (b) and (d), at which most of the indicator is in the aqueous phase and nearly all the surfactant in the organic phase, are unsatisfactory with commercial materials. End-point (a) is rarely used because it gives no warning of its approach. It also has the disadvantage that trace impurities in the indicator, particularly of the oxidation products in methylene blue, may impart a bluish colour to the aqueous layer well before the end-point. The same impurities also interfere in end-point (e) and from our experience we recommend the use of this end-point only with the anionic indicators which are purer and more stable than the cationic ones. This leaves end-points (c) and (f) as the best for cationic indicators such as methylene blue.

It might be mentioned at this point that methylene blue seems to be practically the only cationic indicator that is used for the titration and despite the limitations it seems to be preferred to anionic indicators in most commercial analytical laboratories in the U.K. and abroad. A wide choice of anionic indicators of the sulphonphthalein, sulphonic acid, and fluorescein classes is available, but the vast majority of workers appear to follow closely the technique of the early workers, Barr, Oliver, and Stubbins, and to use bromophenol blue.

Standardisation

At the end of the titration in cases (a) and (e) the whole of the indicator is in combination with surfactant, and a blank correction, which is constant, calculable, reproducible and readily determined, must be applied. In cases (c) and (f) only part of the indicator remains combined with surfactant and the necessary correction depends upon the proportion involved, and this depends in turn upon the relative volumes of aqueous and chloroform layers. Experimental determinations of the blank or of a correction factor have been described by several writers, but for routine analysis it is sufficient to standardise the titrant under similar conditions to those of a determination, thus eliminating the correction. The standard substance in this approach must be of a similar composition to that being determined, which means in many cases that it must contain a mixture of isomers or of homologues as do the commercial materials, and its composition can therefore only be established by other analytical methods, principally by extraction or ion-exchange methods. For *n*-alkyl sulphates, it is possible to prepare the pure materials, and these can be used as standards in this field.

Miscellaneous Factors

After the choice of indicator, of end-point and of standard, that of the titrant is the most important. Cetyltrimethylammonium chloride and cetylpyridinium bromide seem to be most frequently used for anionic detergents.

The stearyl compounds have the disadvantage of lower solubility, while the myristyl and shorter chain homologues may react incompletely. However, we have found that N-alkyl-N-benzyltrimethylammonium chlorides give much sharper end-points than the other two groups of titrant. The stearyl compound again is of low solubility, but the lauryl, myristyl and cetyl compounds all have similar performances and there is little to choose among them except that the cetyl compound, of lowest solubility, is the most readily purified by crystallisation.

Regarding the concentration of the titrant, many workers follow Epton in using titrations of about 10 ml with .004 or .005M titrant, but larger titrations with more dilute solutions, e.g. around 20 ml or .001M as used by Barr *et al* normally give more precise results, and are at least as accurate if due regard is paid to the blank.

All titration procedures are equally suitable for determining anionic or cationic surfactants, the concentration of the other being known, and it is also immaterial whether the solution of unknown concentration is placed in the titration vessel or in the burette, although the former is usually the most convenient.

The single phase titration

The earliest work by Hartley and Runnicles used a single-phase titration of anionic and cationic surfactants, but the end-point with bromophenol blue was not so clear as when the two-phase technique was applied. However, with fluorescent indicators such as eosin¹⁶ and dichlorotetraiodo-fluorescein¹⁸ the end-point may be as sharp as with the two-phase method, and such indicators may repay further study. Their main disadvantage is that large amounts of inorganic salts, and moderate amounts of inactive organic compounds, tend to obscure the end-point.

OTHER METHODS OF ASSAY

Methods based on the formation of an amine salt with anionic surfactants, using an ordinary primary amine, have been used for a long time. One procedure¹⁷ uses toluidine as the amine, extracts the salt with carbon tetrachloride, and determines the amine in the extract by addition of ethanol and titration with alkali. A similar procedure¹⁸ uses benzidine and separates the salt by filtration. The salt may be weighed before titration to give an indication of the equivalent weight, which cannot be determined by any volumetric method.

For determining cationic surfactants, several precipitants containing large anions may be used, and in a review by Chinnick and Lincoln¹⁹, phosphotungstic acid is recommended. Non-ionic surface active agents with an ethanoxyl chain of suitable length for detergency can also be precipitated

with the heteropoly-acids ; phosphomolybdic acid is preferred, as the precipitate can readily be analysed to determine the surfactant content which varies with different compounds. Ampholytic surfactants of the amino-carboxylate group are usually analyzed by the methods employed for cationics, with special attention to reactions in acid solution. Those of the aminosulphonate group are analyzed by the methods used for anionics. Ampholytics containing a sulphate group are subjected to acid hydrolysis to yield an amine which is analyzed as a true cationic compound.

CONCLUSION

A great deal of work on new methods of detergent analysis is being undertaken in this country and abroad, but most of this falls into two classes. The first is a thorough examination of the traditional methods in endeavours to draw up national and international standards, and the second is concerned with new types of detergents, mainly biodegradable anionic surfactants, and a wide range of ampholytics.

Most of this paper has been confined to a discussion of analytical methods that have stood up to the recent scrutiny and that are likely to be issued as standards in the near future.

Among these procedures are two that have hitherto survived severe criticism, but which have such inherent defects that they are liable to be superseded in the second generation of standards. The first is the large group of analyses by solvent extraction. Each operation is limited by an equilibrium partition coefficient and, though series containing up to a dozen extraction and washing steps have been recommended, the overall accuracy and precision of many is barely acceptable. With chromatographic procedures on the other hand, using columns of ion-exchange resins, of alumina, cellulose, and silica, separations may involve hundreds of theoretical equilibrium stages with no more than a few minutes' attention of the analyst. Such methods will become widely used in the future, but a great deal of tedious study is needed before results can be accepted as reliable and reproducible, especially among different laboratories.

The second procedure is the two-phase cationic-anionic titration using methylene blue and this suffers from the same limitations of equilibrium partition as the first method. The best hope for improvement lies in the synthesis of a cationic indicator designed specially for this application. The ideal indicator will probably contain only one basic group, this being a quaternary nitrogen, and will have an intense colour, preferably blue. Nevertheless, an ideal indicator may not overcome the inherent defects of the competing equilibria, for many investigators seem to ignore the extractability of both anionic and cationic surfactants, in the absence of indicator, in solvents such as chloroform. The factors appear to be more serious in

alkaline solutions, which underlines the need for a better indicator that is usable at low pH values.

The other field of much current endeavour is the development of analytical methods to deal with newer types of surfactants. The search for a detergent that is readily decomposed in sewage treatment plants is to a large extent concerned with derivatives of natural fats, particularly of tallow which is available in larger quantities than coconut and palm kernel oils; derivatives are being made and tested at a faster rate than the necessary methods of analysis can be devised. The field of ampholytic surfactants is another in which new compounds are frequently appearing. When commercial considerations have led to a more stable pattern of supply and demand of both types of surfactant, then the analyst can develop procedures that are worthy of publication. This situation is not likely to be reached within the next year or two.

(Received: 27th May 1963)

REFERENCES

Many references given in the first paper below have not been listed again. The books referred to under 4 and 7 below are useful general works, and the former contains a good guide to the literature, excluding the anionic-cationic titration.

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- ⁷ Longman, G. F., and Hilton, J. *Methods for the Analysis of Non-soapy Detergent (NSD) Products* (1961) (The Society for Analytical Chemistry, London)
- ⁸ House, R., and Darragh, J. L. *Anal. Chem.* **26** 1492 (1954)
- ⁹ Voogt, P. *Rec. trav. chim.* **78** 899 (1959)
- ¹⁰ Voogt, P. *Proceedings, 3rd World Congress on Surface Active Agents III* 78 (1960) (University Press, Mainz)
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- ¹³ Silverstein, R. M. *Anal. Chem.* **35** 154 (1963)
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DISCUSSION

MR. G. A. C. PITT : What indicators have you tried other than methylene blue and bromophenol blue ?

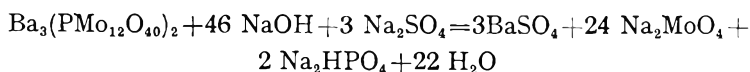
THE LECTURER : Among anionic indicators, methyl orange is the only alternative to bromophenol blue that we have used. A wide range of indicator types is available, but bromophenol blue has so few disadvantages that there is little incentive to look elsewhere. With cationic indicators the situation is quite different, and we have considered every coloured organic cationic compound that has been brought to our attention. Dimidium bromide was mentioned above, and methyl yellow has also been used by us. Indicators such as methyl violet and methyl green gave less satisfactory results than methylene blue ; pinacyanol chloride and methylviologen showed no promise. We think that the problem justifies attempts at the special synthesis of an indicator, and some coloured organic compound containing one quaternary ammonium group and no other ionogenic group in the molecule would probably be suitable.

MR. J. S. LEAHY : Has the use of thin layer chromatography been investigated in place of paper chromatography in the qualitative analysis of detergents ? It would appear to have advantages both in time and possibly conditions of detection.

THE LECTURER : We have not investigated the subject and do not know of any work on thin layer chromatography of detergents. In view of the apparent advantages we hope to look into the technique when time is available.

A MEMBER OF THE AUDIENCE : How is phosphomolybdic acid used ?

THE LECTURER : Phosphomolybdic acid is slowly added to a dilute acid solution of the non-ionic surface active agent and of barium chloride, and the non-ionic compound *M* is thereby precipitated as the complex $\text{Ba}_3(\text{PMo}_{12}\text{O}_{40})_2 \cdot xM$. The precipitate is filtered off, dried, and weighed. The composition of the precipitate is then determined by dissolving a weighed portion in excess of alkali and back-titrating the excess. The overall reaction is :—



For a precise end-point we back-titrate to excess with hydrochloric acid, then add a little neutral sodium sulphate, and titrate again with sodium hydroxide. This reduces the interference due to carbon dioxide, which may be appreciable when soluble barium salts are present. Since 460 ml 0.1N sodium hydroxide are equivalent to 4057 mg of barium phosphomolybdate,

the inorganic content of the precipitate can be calculated. The rest of the precipitate comprises the non-ionic surface active agent the content of which in the original solution is thus determined. An analysis of the precipitate is essential for every new type of non-ionic compound, because the value of x varies from one substance to another, and may even vary among compounds of nominally the same composition.

MR. D. BASS: Your method of analysis for ampholytics is to estimate as cationics under acid conditions. This method works well for the substituted amino acid type, but do you obtain good results using the betaine type of ampholytic? I am thinking in particular of difficulties when there is a degree of internal compensation within the molecule as with the cyclimidinium type.

THE LECTURER: Yes, we find our normal method for cationics to be satisfactory for the betaine type of surface active agent. The two-phase titration is performed in acid solution with chloroform as the organic phase, sodium dodecylbenzenesulphonate as titrant, methylene blue as indicator, and we take complete transference of colour to the organic phase as the end-point.

BOOK REVIEW

Standard Methods of Chemical Analysis. Volume II (A and B). INDUSTRIAL & NATURAL PRODUCTS & NONINSTRUMENTAL METHODS. Sixth Edition. Editor: F. J. Welcher. Part IIA—Pp. xiv + (1-1282) + Ill. Part IIB—Pp. xi + (1283-2613) + Ill. (1963). D. Van Nostrand Company, Inc., New York. \$25 each (not sold separately).

It is almost twenty-five years since a revised edition of *Standard Methods of Chemical Analysis* has appeared. In 1939, the Fifth Edition was published as two volumes but so great have been the modifications, refinements and developments of the methods of chemical analysis since that time that the Sixth Edition appears in three volumes, with Volume II expanded into two parts, bound separately as Volume IIA and Volume IIB. Despite its considerable expansion the purpose of Volume II remains that it shall be a collection of carefully selected well proved methods of technical analysis, of practical value to the professional chemist.

The lay-out of this edition is similar to the previous one, but the expansion due to the inclusion of new material adequately reflects some of the important changes that have taken place in recent years in analytical techniques. The expansion includes chapters on standard laboratory apparatus; detection of cations and anions; mechanical separation; separations by filtration; separations by electrolysis; solvent extraction; separations by distillation and evaporation; chromatography; ion exchange methods in analysis; acid-base titrations in non-aqueous solvents; statistical interpretations; quantitative organic analysis; air pollutants; amino acid analysis of protein hydrolyzates; chemical analysis in clinical medicine; fertilizers; gas analysis with emphasis on vacuum techniques; pesticides; plastics; silicates, glasses, rocks, soils and vitamins.

There are numerous references to original papers and there is a good index at the end of Part B only. It is somewhat annoying that Part B has to be consulted for work that is known to be found in Part A, for these books are not lightweight ones. It is difficult to understand why the index was not included in Part A as well; the book would only be 22 pages larger than Part B had this been done.

Cosmetic chemists may be disappointed that the analysis of cosmetics does not

warrant its own section. In fact the nearest that a cosmetic product approaches such importance is in the section on Soaps and Detergents. Such neglect of the industry, however, does not detract from the value of this volume to the cosmetic analyst for although the products and materials of the so-called heavy industries are well covered, there is an overlap of cosmetic materials in other products. Such treatment makes for interesting reading and may well germinate new ideas in a harassed analyst. Apart from products, the section dealing with techniques and methods provides a large field from which to reap a rich harvest.

T. J. BOWDITCH.

THE SOCIETY OF COSMETIC CHEMISTS OF GREAT BRITAIN

Symposium on The Toxicology of Cosmetic Materials

A SYMPOSIUM on The Toxicology of Cosmetic Materials will be held at the Town Hall, Leamington, Warwicks., on 19th and 20th November 1963. Participation is permitted only when application has been made on the appropriate form, and the fee duly paid. This is £3 3s. for each participant who is a member of one of the Societies of Cosmetic Chemists affiliated to the I.F.S.C.C. The registration fee for non-members is £6 6s. Registration forms, together with full details, can be obtained from the General Secretary, Mrs. E. Millman, 2 Lovers Walk, London, N.3. **The closing date for applications is 22nd October 1963.**

Programme

Tuesday, 19th November 1963

20.00—22.00 Civic Reception by His Worship the Mayor of Leamington, at the Royal Pump Room, Leamington. (Informal dress.)

Wednesday, 20th November 1963

Morning

Chairman: A. HERZKA, Esq., Vice-President.

09.10 Welcome by His Worship the Mayor of Leamington, Councillor F. I. EATON, J.P.
Opening of the Symposium by the President of the Society, S. J. BUSH, F.R.I.C.
Esq.

09.25 "The duty of care and its implications".

L. C. J. BRETT (*Unilever Ltd., London*).

10.00 "Accidental poisoning due to household products".

R. GOULDING, B.Sc., M.D., B.S. (*National Poisons Information Centre, Guy's Hospital, London*).

10.35 COFFEE.

10.55 "Inhalation and toxicity studies".

H. GOMAHN, Dr.Phil., and H. J. KINKEL, Dr.Phil. (*Batelle-Institute e.V., Frankfurt/Main, Germany*).

11.30 "The assessment of safety-in-use: just how much is contributed by feeding studies in animals?"

L. GOLBERG, D.Sc., D.Phil., M.A., B.Chir., F.R.I.C. (*The British Industrial Biological Research Association, London*).

12.05 LUNCH.

Afternoon

Chairman: S. J. BUSH, Esq.

14.00 "Skin reactions to cosmetic preparations".

P. D. C. KINMONT, M.D., M.R.C.P. (*Consultant Dermatologist for Derbyshire Royal Infirmary*).

14.35 "The need for rabbit skin studies in evaluating cosmetic safety".

I. LEVENSTEIN, Ph.D. (*Leberco Laboratories, Roselle Park, N.J., U.S.A.*).

15.10 "The potential irritancy to the rabbit eye mucosa of certain commercially available shampoos".

I. F. GAUNT, B.Sc., and K. H. HARPER, Ph.D., A.R.I.C. (*Huntingdon Research Centre, Huntingdon*).

15.45 Symposium ends, followed by TEA.

1963/64 Programme

Lectures

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

Tuesday, 22nd October 1963

Cosmetic aspects of dentistry

Mr. Thompson, Dental Surgeon

Thursday, 23rd January 1964

The significance of perfumes in toilet preparations

Dr. R. Favre (Proprietary Perfumes, Ltd.)

(Joint Meeting with the British Society of Perfumers.)

Thursday, 27th February 1964

The chemistry of teeth

S. A. Leach, B.Sc., Ph.D. (Unilever, Ltd., Research Laboratory
Isleworth)

Monday, 23rd March 1964

Photomicrography

D. F. Lawson, F.I.B.P., F.R.P.S., F.R.M.S., F.Z.S. (Beecham
Research Laboratories, Ltd.)

Thursday, 7th May 1964

Techniques of detecting allergens

J. G. Feinberg, M.Sc., D.V.M. (Beecham Research Laboratories, Ltd.)

Symposium on Hair

A SYMPOSIUM on Hair will take place in Brighton, Sussex, from the 14th—16th April 1964. Anyone wishing to present a paper is requested to contact the Hon. Organiser, Mr. R. E. Eckton, c/o Givaudan & Co. Ltd., Whyteleafe, Surrey.

Ladies' Night

A DEMONSTRATION of various aspects of beauty culture will take place on Friday, 6th December 1963, at the Royal Society of Arts, John Adam Street, London, W.C.2, at 7.30 p.m.

Annual Dinner and Dance

THIS WILL take place on Friday, 31st January 1964, at the Connaught Rooms, Great Queen Street, London, W.C.2.

TEN VOLUME INDEX

Copies of the Index for Volumes I—X (1947-1959) are still available at Sw.Fr.10 per copy, from the

Swiss Society of Cosmetic Chemists,
7, place de la Fusterie,
Geneva,
Switzerland.

GENERAL NOTICES

Publication dates : The "Journal of the Society of Cosmetic Chemists" is published monthly.

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

One issue by the Gesellschaft Deutscher Kosmetik-Chemiker, e.V.
from Hamburg-Grossflottbek, Beselerstrasse 1, Germany.

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3rd INTERNATIONAL CONGRESS OF COSMETIC SCIENCE

THE 3RD CONGRESS of the International Federation of Societies of Cosmetic Chemists is being organised by the Society of Cosmetic Chemists, and will be held in New York from 21st—28th June 1964.

The American Society chose New York City because the World's Fair will be held there at that time, and Thursday, 25th June 1964, has been designated as Cosmetic Chemists' Day.

The Congress will be held on the campus of Columbia University. Anticipating that accommodation in New York during the World's Fair will be costly and scarce, the Society of Cosmetic Chemists has reserved rooms for participants in New Hall, the newest residence hall on the campus which is built, and will be operated, like a hotel during the Congress.

SCIENTIFIC PROGRAMME

The Congress will have four morning sessions, Tuesday to Friday, 23rd—26th June 1964.

Seminar Areas

(a) *Safety Aspects of Cosmetic Usage.*

- (1) Review of recent clinical experience.
- (2) Advanced techniques for testing *in vivo*.
- (3) Regulatory aspects.
- (4) Statistical aspects.

(b) *Instrumentation's Role in Cosmetic Research and Control.*

- (1) Chromatography :
 - (a) Gas chromatography.
 - (b) Paper and other absorption media.
- (2) Spectroscopy.
- (3) Electron microscopy.

(c) *Cosmetics versus Skin Ageing.*

- (1) Physiology and biochemistry of the skin ageing process.
- (2) Radiation effects.
- (3) Action of steroids.
- (4) Atmospheric and environmental effects.

(d) *Cosmetics and Micro-Organisms.*

- (1) Preservation.
- (2) Control of skin flora.
- (3) Microbial aspects of hair and scalp problems.
- (4) Antibiotics versus antiseptics in cosmetics.

ACCOMMODATION

Through the generosity of the American Society of Cosmetic Chemists, members of the Society of Cosmetic Chemists of Great Britain, or of any other Society of Cosmetic Chemists affiliated to the I.F.S.C.C., will be admitted free of charge to the Congress under the "Package Deal", subject to the availability of accommodation. All reservations must be accompanied by a deposit which will be returned upon arrival at the Congress, or will be refunded up to 15th May 1964.

TRAVEL ARRANGEMENTS

Arrangements have been made for members to travel with a special flight of Aer Lingus Irish Airlines, in a Boeing 707 jet aircraft. The cost from **London** to New York and return, will be **£75** per person, and from other **European centres**, approx. **£85** to **£95** per person, irrespective of age.

The departure from London is on the morning of 21st June 1964, thus arriving in New York during the afternoon (travelling time approx. 7½ hours). The return flight, which will last 6½ hours, is scheduled to leave New York between 7th and 12th July 1964, depending on the wishes of the majority of the participants.

Participants must also return as a group and the free baggage allowance is 44 lb.

A deposit of £10 must accompany each booking.

Registration Forms

Anyone interested in coming to the Congress, is asked to complete the attached coupon without delay, and to send same to the Hon. Travel Organiser.

SOCIETY OF COSMETIC CHEMISTS OF GREAT BRITAIN

3rd International Congress of Cosmetic Science

New York—23rd to 26th June 1964

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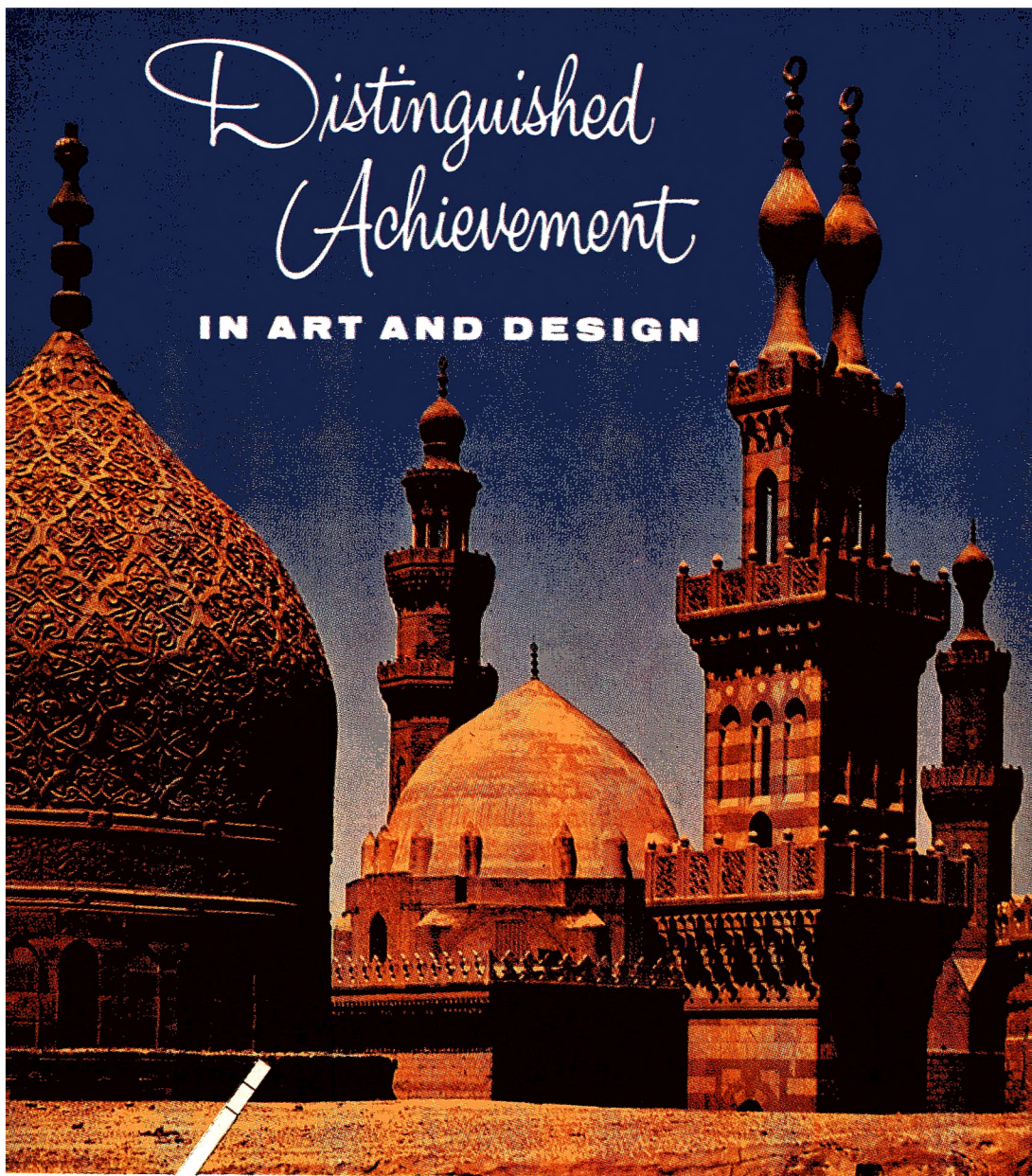
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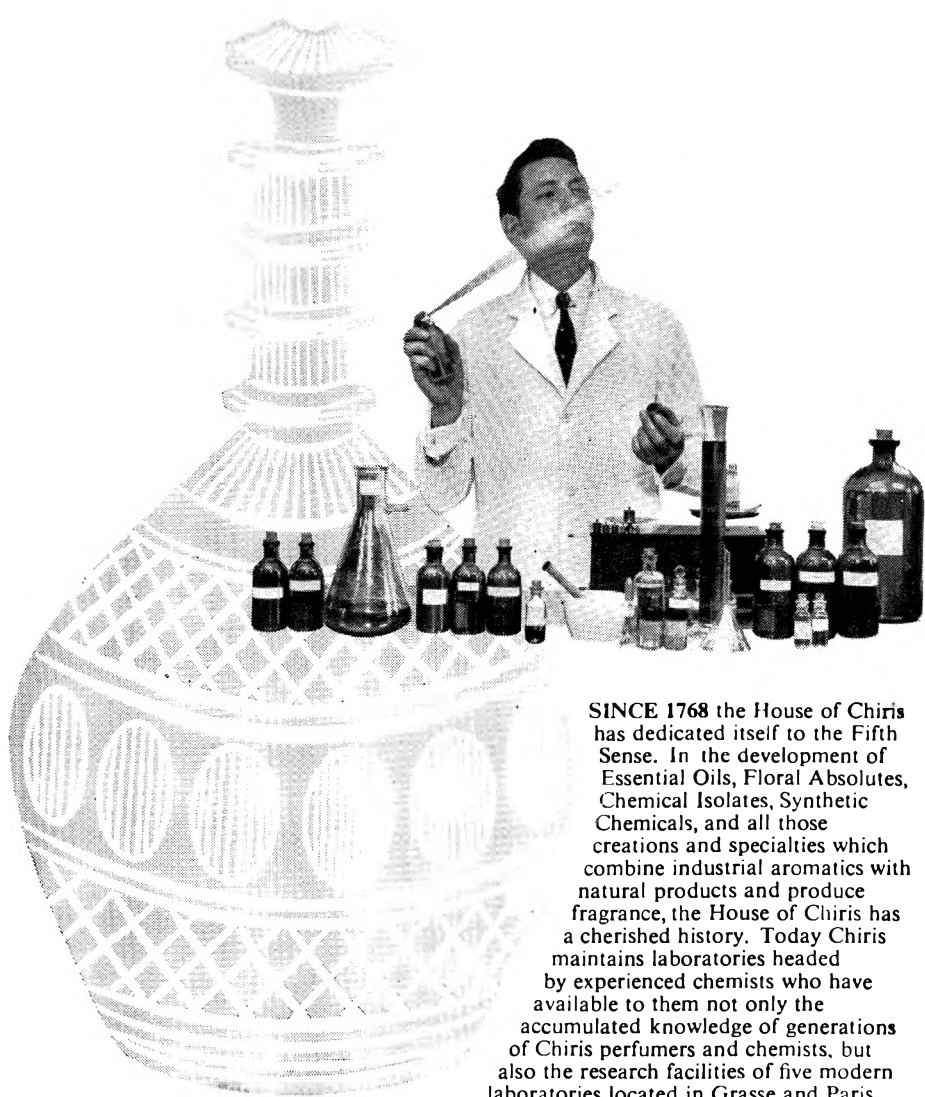
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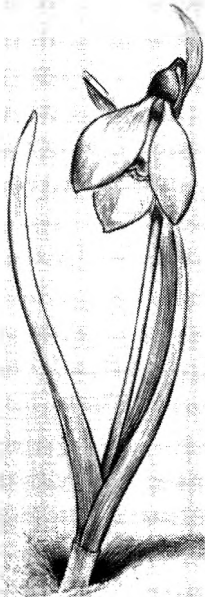


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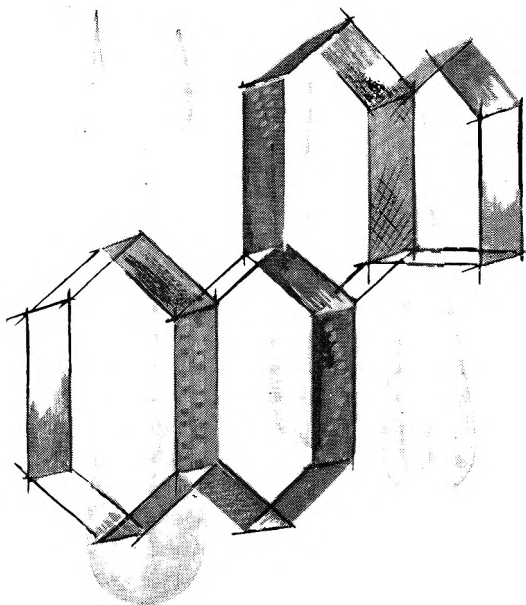
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The journal is intended to provide a wide-ranging service of abstracts and general articles on food and cosmetics toxicology. It will also aim at complete coverage of changes in legislation relating to food additives whether direct or adventitious. Food and cosmetics toxicology is primarily intended for the use of food scientists and technologists, manufacturers, administrators and legislators who neither read nor have access to the medical, pharmacological, or toxicological literature. In addition the journal will constitute a medium for the publication of reviews and original articles relating to the fields of interest covered by the British Industrial Biological Research Association.

The fundamental object of the journal will be to disseminate as widely as possible the ideas and principles for which B.I.B.R.A. stands, by bringing home to everyone concerned with food and cosmetics, in whatever capacity, the new knowledge of toxicology and the responsibilities to the public which that knowledge imposes.

The dominating theme will be the need to foster technological progress in the amelioration of human malnutrition. An indissoluble part of such progress is the objective of better and safer additives at every stage in the production, processing, packaging and distribution of food in every country, large or small. The emphasis on safety-in-use of additives must not lead us to ignore the importance of recognizing, identifying and eliminating naturally-occurring toxic and carcinogenic materials from human and animal diets. In the interests of international co-operation it is important to eliminate legislative barriers to international trade which arise from different permitted lists of food additives, and the new journal will be dedicated to this end.

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