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SOME ASPECTS OF THE SAFETY OF AEROSOL CONTAINERS

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

The relevant considerations and appropriate laboratory tests, which support official advice on the safe transportation of aerosol dispensers, are set out. Attention is given to the construction and performance of containers and protective caps, with particular reference to the effect of elevated temperature and pressure. The hazards associated with the nature of concentrate and propellants are examined in detail.

INTRODUCTION

RECOMMENDATIONS on the *carriage of dangerous goods by sea*, which are accepted by the Ministry of Transport as meeting the requirements of the Merchant Shipping (Dangerous Goods) Rules, 1952, are contained in the Report of the Standing Advisory Committee on the Carriage of Dangerous Goods and Explosives in ships, commonly known as the "Blue Book"[1]. In Section 10, "Other Dangerous Goods", there is an entry requiring all proposals for shipment of aerosol dispensers to be referred to the Ministry of

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Note: Throughout this paper, unless specified to the contrary, all temperatures are expressed in degrees Centigrade (Celsius), and all pressures in atmospheres absolute.

Transport. As part of the analytical and advisory service offered by this laboratory, samples of all such dispensers are examined and the Ministry's Marine Safety Division is advised on suitable packing, conditions of stowage and labelling, within the bounds of any existing precedents and Standing Advisory Committee recommendations.

The regulations of the International Air Transport Association relating to the *carriage of Restricted Articles by air*[2] require aerosol dispensers to be classified according to the hazardous nature of the contents, including propellant(s), if they come within the definitions in the regulations. In doubtful cases, we have given advice to the Ministry of Aviation or, on occasion, to the national airlines directly. Classification of aerosol products is a problem constantly exercising the I.A.T.A. Permanent Working Group on Restricted Articles but, thus far, differences in national standards have prevented agreement on definite performance requirements.

In addition to these two areas of responsibility, views are exchanged with British Railways Board technical staff, particularly concerning carriage on rail ferries. The laboratory has, until recently, examined dispensers submitted for certain War Office (Chief Provision Office) Service Contracts. Here the concern has been primarily with storage and use under somewhat rigorous conditions. Otherwise, for civilian use, the laboratory is not directly concerned with retail/wholesale storage, nor the functioning of aerosols dispensers, but nevertheless has an interest in these matters arising from service on the relevant British Standard Container Committee. Quite independently, our Customs Division examines samples of imported aerosol dispensers ; whilst their interest is confined to the presence of dutiable constituents, any unusual feature in foreign container design is brought to the author's attention.

Table 1

Year :	1950	1951	1952	1953	1954	1955	1956	1957	1958	1959	1960	1961	1962
(i)	3	0	2	1	7	2	9	7	8	14	45	142	163
(ii)	0·5	1·25	1·5	2·0	2·5	6·0	8·0	12	17	27	50	55	65

(*i*) cites the number of different aerosol dispensers examined annually in the Government Laboratory in connection with the Carriage of Dangerous Goods by Sea.

(*ii*) shows the rate of increase of U.K. home sales of such dispensers expressed in million units ; data to 1956 is taken from Herzka[3].

Records of the examination in this laboratory of pressurized containers extend back to at least 1950. But, as will be apparent from *Table 1*, there has been a dramatic increase in the diversity of pressurized products on which our advice has been sought in the last three years ; this rise reflects the steady increase of the home sales of these products. However, whilst it has been held desirable that every encouragement should be

given to boosting the exports of this country, advice suggesting any relaxation of stringent safety recommendations for the carriage of Dangerous Goods can only be offered after a very careful scrutiny of the potential hazards offered in transit. This advice in special circumstances may depend upon prevailing climatic conditions appropriate to a given journey or occasionally to a feature of a particular ship but, in general, one considers the construction of the container, any hazardous properties of concentrate and propellants and then the packing proposed. A series of *ad hoc* laboratory tests have been evolved to support such an investigation, and these are discussed below.

Assessment of the Container

Dispensers submitted to this laboratory have been constructed of aluminium, metal- or plastics-coated glass, tinplate or blackplate.

Prior to 1956, with one exception, all samples examined comprised an extruded *aluminium*, seamless ("monobloc") container with one flat, pressed end, and a standard valve insert crimped in the other; capacities varied between 1 and 6 fl. oz. This type appears to be the container of choice for the smaller sizes. An alternative series of larger (4, 6, 12 and 20 oz) dispensers have an aluminium case, double-locked to a non-integral dished tinplate base; the 12 and 20 oz varieties seem still to be popular. Corrosion from products containing the lower alcohols can be avoided by one- or two-coat internal lacquering, although this is appreciably more difficult to apply for the extruded cases; *iso*propyl alcohol is said[4] not to be corrosive in the absence of water.

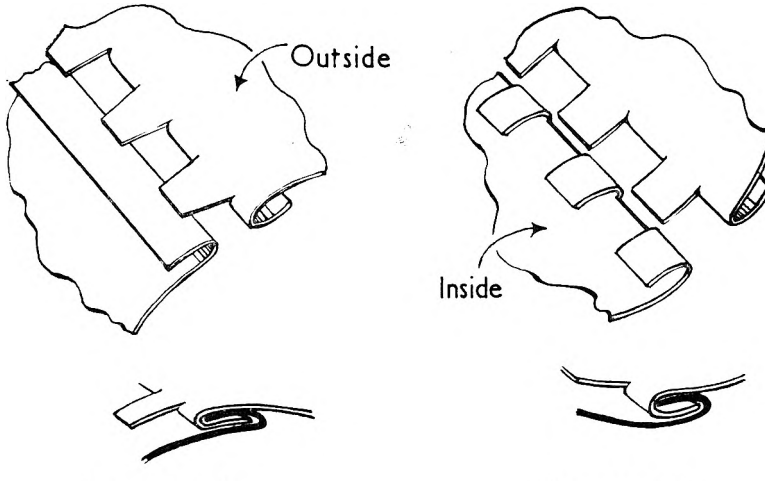
Glass containers have been used for cosmetic or pharmaceutical preparations where contact with metal has to be avoided. They are considered to be very hazardous unless the glass is protected by a metal case (generally extruded aluminium; externally lacquered if a luxury product) or a thick, coloured, plastic skin that retains the fragments if the glass were to shatter. Such a skin is usually formed from a polyvinyl chloride resin. One of this type was first submitted in 1957; since then, 12 more have been examined for carriage by sea purposes. A much larger variety of glass dispensers covered and uncovered, have been imported from Europe and North America; these include pressurized glass containers that are intended as "refills" for relatively costly outer metal cases. A recent innovation, already popular in the U.S.A., is the so-called "purse-spray"—a thick-wall glass container of about 6 ml capacity, fitted with a lacquered valve seating and a polyethylene actuator. This miniature dispenser is protected by an outer cellulose-ester case and polystyrene cap. The spray is rapidly discharged, and may subsequently be refilled from a larger dispenser, with which it is sold in so-called "mother and daughter packs".

One European insecticide dispenser examined in 1955 comprised a case of lacquered *blackplate* (0·24 mm thick), locked to coated tinplate, dished, crown and base.

The great majority of dispensers examined by us since 1957 have been exclusively of electrolytic *tinplate* construction, that is to say comprising a tinplate case with locked soldered side-seam and non-integral tinplate ends, the dished base being attached by a double-locked seam and the (standard) valve insert crimped into the domed upper end. Nominal capacities of 6, 8 and 12 oz are the most frequently met with, but 16 oz containers figure in 8% of the applications. Two varieties of locked side-seam are seen ; the older type comprises an upper lip that is alternately tongued and hooked, the hooks engaging with a continuous curl on the under lip. The locked hooks and lapped tongues then form the soldered seam, which, for convenience, will be referred to as "seam O". An alternative seam, "A", now gradually superseding the other, was first noted by us in a series of specimen containers submitted by arrangement with the Metal Box Co. in October, 1960 ; this special investigation is discussed below. With seam "A", both lips are alternately tongued and hooked ; the two sets of hooks engage and are soldered but the upper tongues have been excised, leaving an externally apparent butt joint that is supported by the lapping of the lower alternate tongues. Both types of seam are illustrated in *Fig. 1.*

FIG. 1

DETAILS OF JOINTS OF CONTAINERS



It is believed that tinplate dispensers are cheaper and easier to fabricate and that, further, they are less likely to be corroded by formulations containing the lower alcohols. Thus ethanol containing not more than 1·5% of water has no significant corrosive effect after a year at 25° [4].

Hot storage tests. There is concern not only that a container is properly constructed and has been properly purged and filled, but also that a dispenser containing a given formulation shall withstand prolonged exposure to the most critical conditions likely to obtain during storage and transport. To this end, a standard hot storage test has been evolved in the past decade by this Laboratory. The earliest procedure was similar to that required by the War Office (CPO) Specification which required that every filled dispenser should be tested by immersion in a water bath at 71° for at least three minutes. The 8th revision[5], requires in addition that an agreed number of the filled containers are maintained at this temperature for 20 minutes to observe any sign of leakage, distortion or other deterioration. There is also a rough usage test, wherein a filled container is permitted to fall 30″ onto a hardwood surface so as to receive impact, in turn, on both ends and its side. It is understood that usually aluminium containers have been found acceptable for these contracts.

A 1952 Laboratory report refers to the absence of weight loss following "prolonged storage" at 70°, whilst the next year a four-day storage test in an oven at 35° was employed. In 1955, two days at 55° were favoured, partly following the American adoption of this temperature for (brief) immersion tests. Since 1956 for transport evaluation, this Laboratory has consistently adopted the practice of examining containers before and after 18–24 hours' storage within a protective case in an oven maintained at 55°. It is believed that this test offers a realistic trial of a dispenser that is to be carried by sea through the tropics and effectively simulates the container fatigue experienced in a 6 day cycle of 3 to 4 hours exposure at 55°. Where an application has referred specifically to carriage in temperate latitudes, the containers have been stored for a similar period at 45°. "Temperate latitudes" has normally been interpreted as North Atlantic and North European waters; special consideration is given to conveyance in the Mediterranean, which is outside the tropical limits of Ref. 1 (page 5).

It might appear that the adoption of a *test temperature* of 55° was somewhat arbitrary; in the sense that it represented a consensus of differing opinions, it was. Thus, successive (DSIR) Gas Cylinder Committees have expressed opinions concerning the maximum temperature to be assumed for temperate and tropical climates[6]. First (1918), it was recommended that 45° and 65°, respectively, should be adopted, whilst their sub-Committee on Welded Containers recommended 50° and 70° respectively, considering that "the increased seriousness of the consequence which might follow the failure

of a large container compared with a solid-drawn cylinder justified the adoption of a greater margin of safety". The 1935 Committee assumed a general working pressure in tropical climates calculated for 65° except for "some countries where higher temperatures were known to be attained by containers on occasion". The Home Office Committee (appointed in 1946; Draft Report[6]), considered the excellent safety record over a considerable period consequent upon adoption of these previous temperature recommendations, and also the complexity of precise calculations of maximum temperature attainable by a container based on meteorological data. They therefore recommended the retention of the 45° and 65° assumptions, in general, with two reservations: (i) in countries where "the contents of a cylinder or container will reach a temperature in excess of 65°" local requirements should be observed; (ii) based on U.K. experience with large road tankers on short haul (36 hour) journeys, it is recommended that for "large welded containers, exceeding 3 feet in diameter and intended for the conveyance of non-toxic gases, the assumed maximum temperature in temperate climates should be (reduced to) 38°".

These values of 45° and 65° have generally been followed by the Ministry of Transport, in the absence of sufficient meteorological data, but specific concessions have occasionally been made. Thus, experience of tropical storage of welded drums suggested that 45° gives an adequate margin for calculation of ullage, when allowance is made for thermal expansion and elasticity of the drum itself. (These considerations are not applicable to filled built-up containers, such as the side-seam aerosol dispensers, where the onset of solder creep lessens the effective elasticity above about 50°). Inert, low pressure, liquefied gases may be accepted in drums tested only up to 45°, provided these are stowed under deck. In the U.S.A., a maximum temperature of 54·4° (i.e. 130°F) is employed in the regulations of the Interstate Commerce Commission and this value has been adopted in the shipping section of the Code of Federal Regulations. It was the I.C.C. regulations that first required the water-bath immersion test (at 130°F) for all filled containers (or a representative selection if this test would damage the contents). The I.A.T.A. regulations[2] (p. 58) refer to a range "in the order of —40° to +54·4°" as the "extremes of temperature which might be encountered in international transportation", both in flight and ground storage. Some meteorological data for seaborne freight have been quoted[7] by Holler, of the German Maritime Weather Bureau. Thus, in the Red Sea, cargo space maxima of 35° (lower hold), 44° ("'tween deck"), 51° (outside) and 65°, or even 70° (unshaded deck cargo); a maximum diurnal variation of 12° was recorded off the Gold Coast.

Results of hot storage tests for the years 1950-56, in which one lacquered ironplate and 22 seamless aluminium aerosol dispensers were examined,

record only one (aluminium) container failure, and that due to leakage around the valve seating following 18 hours' storage at 70°. Subsequently, there have been slight leakages (less than 2%) from one aluminium (out of 66 applications) and one PVC-coated glass dispenser (from 13); two samples of one of the latter group of containers leaked extensively from a badly seated valve but subsequent samples have been satisfactory. In the same period (1957-62), one or more samples of dispensers submitted with 30 applications (out of 300 utilizing tinplate containers) have leaked extensively following 18 hours' storage at 55°; two of these cases exploded, one violently. In eleven other applications, containers showed slight leakage (less than 2%) and samples of three more suffered inversion of the inwardly dished base to assume a convex conformation, without loss of contents. However, 29 of the 30 dispensers with tinplate cases that failed, possessed the commoner locked side-seam referred to a seam "O". Subsequent examination of such containers usually shows that the hooked portions of the seam have eased, the soldering fractured and the contents have been forced out. At least 4 cases suffered inversion of the dished base prior to the easing of the seam, and with another sample the crimped shoulder of the domed top was uncurled,

RESULTS OF STORAGE OF AEROSOL DISPENSERS AT ELEVATED TEMPERATURES

Table 2. Applications for carriage by sea

	Container								Total	
	Aluminium		PVC/glass		Tinplate					
					Seam "O"		Seam "A"			
	test	fail	test	fail	test	fail	test	fail	test	fail
1950	3	0	0	0	0	0	0	0	3	0
1951	0	0	0	0	0	0	0	0	0	0
1952	2	(d)	0	0	0	0	0	0	2	(d)
1953	1	0	0	0	0	0	0	0	1	0
1954	7	1	0	0	0	0	0	0	7	1
1955	1	0	0	0	0	0	0	0	2*	0
1956	8	0	0	0	1	0	0	0	9	0
1957	3	0	1	0	3	0	0	0	7	0
1958	2	0	3	(s)	3	0	0	0	8	(s)
1959	2	(s)	2	0	10	0	0	0	14	(s)
1960	9	0	3	(s)	33	3 (s)	0	0	45	3 (2s)
1961	14	0	0	0	121	22 (2d, 3s)	7	0	142	22 (2d,3s)
1962	36	0	4	1	56	4 (4s)	67	1 (d, 3s)	163	6 (d, 3s)
Total	88	1 + (d, s)	13	1 + (2s)	227	29 + (2d, 8s)	74	1 + (d, 3s)	403*	32 + (4d,14s)

* includes one lacquered ironplate container.
(d) dished base inverted but no leakage.
(s) slight leakage but no visible damage.

but in many other instances the seam has proved the weakest factor. In only one sample from 74 examples of dispensers incorporating the "A" type locked side-seam has the seam failed in the hot storage test ; in this instance the gauge pressure, recorded at 21° after storage, was not excessive and the formulation was not significantly hazardous *per se*. There has also been one occasion when an "A" seam dispenser showed incipient dimpling of the dished base. This record itself indicates the greater strength of the "A" seam when compared with the "O" type. Our experience with the heat storage of aerosol dispensers is summarized in *Table 2*, and typical casualties are illustrated in *Fig. 2*.

Figure 2

When the results of storage tests at elevated temperatures are compared with hydraulic tests, an interesting distinction emerges. In the latter tests, partial relief of pressure ordinarily follows the sequence:

(i) dimpling, leading to inversion of the dished base;
(ii) uncrimping of the can shoulder;
(iii) easing of the valve seating, and finally,
(iv) fracture of the side-seam.

During hot storage, however, the first evidence of failure is, most frequently, an easing of the "O" type soldered side-seam.

Following a report to the Ministry of Transport in October 1960 on the failure of a number of locked side-seam tinplate containers, The Metal Box Co. Research Department kindly provided three groups of a dozen tinplate containers in order that we might contrast their performance when stored at an elevated temperature. One group (of 6 oz capacity) was sealed with the (then) novel internally-locked seam, which we have referred to as seam "A", and the other two groups comprised 6 and 12 oz dispensers with the common seam "O". All had the normal crimped shoulder valve insert with the actuator button protected by a sturdy tinplate cap. Within each group the dispensers were filled with a series of propellant mixtures, viz. 50:50, 55:45, 60:40 and 65:35 proportions of propellants 12 and 11. Two containers for every mixture within each group were stored for 18 hours at 55°: the complete results are shown in *Table 3.* Considering first the 65/35 mixture which contained the highest proportion of lower boiling (—29°) propellant 12 : two-thirds of the contents of both 12 oz and all of one 6 oz, seam "O" dispenser had evaporated ; the soldering on all three containers had failed, raising the tongues, revealing hair line cracks, where the hooked segments had eased, and displacing appreciable amounts of flux. About half of the contents of one seam "A" container also had evaporated but there were no obvious signs of damage ; one each of the 6 oz seam "O" and "A" dispensers resisted leakage of propellants during these short term tests.

Table 3. Special Investigation
Percent nett weight lost following 18 hours' storage at 55°

	Seam / Container size	A 6 oz	O 6 oz	O 12 oz
mixture of propellants 12 and 11	50:50	0	0	0
		45	0	0
	55:45	0	5	0
		0	0	65*
	60:40	0	0	0
		0	0	0
	65:35	0	100*	69*
		46	0	68*

* structural faults apparent.

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Only two dispensers containing one of the other three propellant mixtures showed any significant weight loss. One 12 oz seam "O" container lost $\frac{2}{3}$ of its 55/45 mixture and one seam "A" dispenser lost 45% of the 50/50 propellant ratio, the former exhibited the same forcing of the tongued seam "O" and spreading of the flux, whereas the seam "A" dispenser appeared still to be intact.

A workshop examination, after unsoldering the seams of the opened containers, showed the essential difference between the common "O" and the novel "A" type (*Fig. 1*). Comparison of the two seams suggested that the "O" type might offer better resistance to crushing, whilst the "A" seam could be expected better to resist internal pressure, although it was considered arguable that the discontinuous hooking of the latter might prevent much lateral transmission of thrust between the tongues. In the absence of specialized knowledge of the can manufacturing industry, it was difficult to comment further; presumably it is easier to prepare and solder the continuous curl of the common "O" seam, but the "A" seam has now begun largely to replace it. It is understood that the U.K. manufacturers have incorporated the "A" seam in all their new containers. Experts in the industry might care to comment on a possible compromise seam, that is the reverse of the "O" type, i.e. with a continuous curl on the outer lip engaging with alternate hooks on the inner lip, the outstanding (inner) tongues being lapped as in the "A" seam.

Pressure tests. If all filled containers have been submitted to a brief production-line immersion test in which the (gaseous) contents reached 55°, the possibility of over-filling (resulting in inadequate ullage and higher pressure) and incomplete purging of air (higher pressure) should have been eliminated. However, having regard to the high rate of failure experienced in 1961 (one or more container in about one application in six with the "O" seam), it was considered useful to check the gauge pressure of each formulation before and after exposure to the hot storage test. These measurements are conveniently made after equilibriation in a bath maintained at a suitable reference temperature (e.g. 21°). More recently, pressures have also been measured at 55°; after 18 hours, one of the three dispensers under test is transferred to (another) water-bath at 55°. Standard bronze tube gauges (0–100 and 0–250 psi) have been fitted with PTFE sleeve adapters, the internal diameter of which corresponds to the commoner (4·1 mm) valve stems; for the finer (3·25 mm) stems, a suitable intermediate sleeve may be formed from a short piece of standard dip tube.

Such measurements are a useful supplement to storage tests, but ideally the suitability of a container should be established beforehand. Thus, hydraulic tests on daily production samples at the container factory can confirm a ceiling pressure. After allowance of an appropriate safety margin

(perhaps varying with the implicit hazardous properties of the fill), the suitability of a container is then simply related to the total vapour pressure ("effective working pressure" or EWP), determined at ambient and at maximum temperature, of an intended formulation. Considerations such as these are being examined by the relevant B.S. committee, and already exist in the substantive or draft regulations of a number of other countries.

The EWP at 50° is limited in Finland to 11·6, and in Germany it was 6·2, atmospheres (atm), although the latter was being reconsidered[4]. In the Union of South Africa, the EWP at 55° for glass and plastics dispensers must not exceed 8·5 atm, or for metal dispensers, 12·2 atm. In a recent Swedish draft, three grades of dispenser are related to six groups of aerosol formulations and also for butane fuel containers ; the groups are based on EWP's at 21° of 3 atm, 3 to 4·2, 4·2 to 5 (if non-toxic, non-combustible), up to 6 atm for insecticides pressurized by a non-combustible compressed gas, up to 6·3 (at 21° and 8·7 at 55°) for a non-toxic non-combustible concentrate pressurized by a compressed gas and, finally, food or soap products with a compressed gas with EWP's of 7 and 9 atm at 21° and 55° respectively. There is also an over-riding limit of 12 atm. In the U.S.A., a somewhat similar system of classification is employed : for EWP's measured at 21°, no regulations apply below 2·7 atm, but above this value three ranges are listed : 2·7 to 3·7, 3·7 to 5 and 5 to 5·8 atm. For the two higher ranges, a particular container is specified. As will be apparent from *Fig. 3*, propellant 12 has a vapour pressure at 21° of 5·7 atm, rising to about 13·5 at 55°, from which it may be inferred that the extrapolated U.S. maximum EWP is higher than that allowed in the other countries mentioned.

A specified proportion of dispensers (e.g. 1 in 5,000) are tested hydraulically prior to filling : Sweden (minimum test 12 atm) and Finland require pressures 1½ times the estimated EWP at 50°, and Germany a standard 9·7 atm. The Union of South Africa tests all "low pressure" containers at 9·6 atm and medium pressure (metal only) dispensers at 13·2 atm, whilst 1 per 5,000 is expected to resist 12·2 or 15·3 atm, respectively, when tested to destruction. Sweden require a similar test to destruction (for 1 in 5,000 containers) which must resist at least 18 atm. The five countries mentioned test all filled containers by immersion in a waterbath until the contents reach the temperature of 55° (Finland 50°). In addition to the waterbath test at 71°, the CPO specification[5] requires a container to withstand 17 atm.

Concentrate

Whilst it is possible to draw certain general conclusions as to composition from the function and details specified on the maker's label, if the potential hazards of the filled dispenser are to be assessed properly, it is imperative that the manufacturer or his agent supply, in confidence, a complete quantitative

declaration of the composition. In default of such information, a complete analysis of the concentrate is a time-consuming and expensive business which might inordinately delay a decision on a particular application. The supply of inaccurate or wilfully misleading details could result in very serious consequences if an accident subsequently occurred. Normally, such a declaration is accepted, subject to elucidation of any inherent uncertainty, but where the performance tests (see below)—which will in part be based upon this declaration—indicate any inconsistency, the containers are cooled to —30°, when (unless compressed gases are suspected) the dispensers may safely be cut open and the contents examined. The chilled product is fractionally distilled, and the components identified chemically, by ultra-violet and infra-red spectroscopy and by gas-chromatography.

Of the four principal hazards, *flammability* is considered the most serious and certain routine performance tests are invariably applied. The first test is concerned with the emitted spray, i.e. the resultant flammability of the mixture of propellant(s), solvent(s) and active ingredients ; this test corresponds roughly to the U.S. Bureau of Explosives flame projection test. A lighted taper is applied from above and from the side of the aerosol spray at distances of approximately 50, 25, 5 and 1 cm from the valve button ; an estimate of the flame projection is made and any tendency to strike back to the jet noted. Ethanolic concentrates typically show strong projection at 5 cm, becoming progressively diffuse and weak when tested at 25 and 50 cm. The test is repeated after shaking the container vigorously (for about 30 seconds) and again with the container inverted. Where a flammable (hydrocarbon) propellant is indicated, by declaration and/or the observed flammability of the spray of the inverted dispenser, the dispenser is discharged within a confined space (a litre beaker, over which a clock glass may be slid, is conveniently employed) and a lighted taper applied : a strong flash is observed when (say) butane is present. This small-scale qualitative test for the formation of an explosive mixture with air, although arbitrary, may be compared with the U.S. "closed drum" test. A second sequence of tests determines the combustibility of the residual components following successive evaporation of the more volatile constituents. The dispenser is discharged into an open (porcelain or silica) dish until up to 15 ml of liquid have been collected, and a lighted taper promptly applied. If the liquid fails to ignite, the test is repeated successively after $\frac{1}{2}$, $1\frac{1}{2}$ and 5 minutes (at laboratory temperature), after 5 minutes cooling following 2 minutes heating on a boiling steam bath and finally after a further 5, and then 10, minutes heating (being tested whilst still on the steam bath). This performance test on the concentrate is more searching than the U.S. (modified Tagliabue open cup) test but still makes (practical) allowance for the masking or suppression of flammability by the presence of a "quenching" component of comparable

volatility. Details of the three American aerosol flammability tests referred to above, are to be found elsewhere[4,8].

The results of these performance tests are compared with the declared composition and published values for any flash point of these compounds. Where any inconsistency is revealed, the product is examined as described earlier. Normally, small amounts of lower flashing constituents are disregarded for the purpose of assigning stowage restrictions where the performance tests appear to justify this course.

No specific laboratory tests are undertaken in connection with the potential *toxicity* of a formulation. Each component, in its declared proportions is considered in terms of published data, concerning acute and chronic doses, and information available within this and related laboratories ; in the absence of such knowledge, the industrial safety record is examined or, occasionally, the experience of a known manufacturer of the particular ingredients may be sought. In assessing the danger of volatile toxic liquids, in addition to

Table 4
Volatile haloalkanes in order of increasing toxicity.

	MAC (8 hour day)		Lethal Conc. (mice)		
	ppm	g/m³	%	g/m³	b.p.
Propellant 12	1000	5·0	—	—	−30
Propellant 11	1000	5·6	10	560	24
Ethyl chloride	1000	2·6	—	—	12
Methylene dichloride ..	500	1·8	1·4	50	40
Methyl chloroform ..	500	2·7	1·1	65	74
Trichlorethylene	100	0·52	0·8	42	87
Tetrachlorethylene ..	100	0·67	0·6	40	121
Methyl chloride	100	0·21	—	—	−24
Chloroform	50	0·24	0·6	28	61
Carbon tetrachloride ..	25	0·16	0·9	60	77

Table 5
Pesticide components commonly used in aerosol formulations, in order of increasing acute toxicity. Expressed as the mean oral dose (g/kg body weight) lethal to 50% of a group of rats.

Pyrethrins	1·0
Malathion	0·9
2,4-D	0·6
DDT	0·6
Lethane	0·5
Chlordane	0·4
BHC (lindane)	0·2
Pentachlorphenol	0·2
Toxaphene	0·1
DDVP	0·06
Aldrin	0·05
Dieldrin	0·05
Parathion*	0·004

* quoted for comparison purposes.

values for lethal concentrations and vapour pressure data, internationally accepted "Maximum Allowable Concentrations" may be considered. The relevant stowage precautions are discussed in a later section, and some toxicity data are quoted in *Tables 4 and 5*.

There are two aspects of the *corrosion* hazard. The product may be incompatible with its dispenser, causing leakage in transit, and there is also a risk from the occasional potentially corrosive formulation in a suitable container if leakage occurred for any other reason. The former point should have been thoroughly covered by the product research prior to manufacture and subsequent long-term storage tests; such tests cannot be reproduced in a short term enquiry. Further, it has been stated[4] (p. 171) that corrosion may even be inhibited during elevated temperature storage tests, yet be apparent after briefer priods at ambient temperatures. Thus, for the purposes of carriage by sea applications, it must be accepted *de facto* that the manufacturer has developed a suitable container for his product unless there is apparent evidence to the contrary.

However, on the second aspect, wherever the declared composition indicates the presence of significant amounts of an ingredient known to be appreciably corrosive, the rate of attack of the residual liquid of the formulation on standard pieces of burnished mild steel plate exposed at 20° and 55° is determined. If subsequent examination reveals no signs of pitting or other non-uniform attack, the average penetration is calculated from the weight loss and expressed either as "*ipy*" (inches penetration per year) or, where attack only on one unprotected surface or a special substrate is concerned, as "*mdd*" (mg/dm²/day).

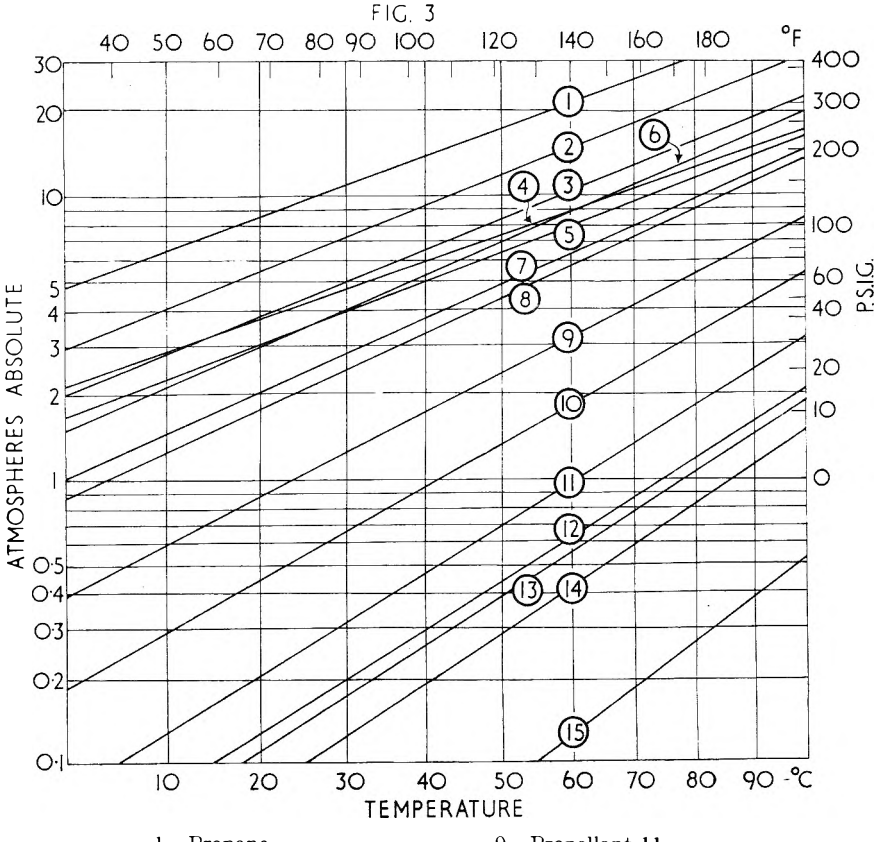
If from the declared, or subsequently derived, composition, chemical intuition or precedent suggests that there may be *chemical or physical interaction* between one or more of the constituents and adjacently stowed cargo, then appropriate stowage restrictions are recommended. One normally required restriction deals with the juxtaposition of strong acids (for tinplate containers), and both strong acids and alkalies (for aluminium containers) which might, if spilt, attack the dispensers and release their potentially hazardous pressurized contents. It should be noted that, in general, both solvent and active principles in the aerosol formulations may contribute to any or all of the four hazards that have been described in this section.

Propellants

There is a reference in an 1889 patent to methyl and ethyl chloride as liquefied gaseous propellants in a spray, and prior to 1933, carbon dioxide, dimethyl ether, *iso*butane and vinyl chloride had all been suggested for similar purposes. Chlorinated fluorinated hydrocarbons, having been

produced for use as refrigerants, were in 1934 recommended both as extinguishant and propellant in a fire quenching system and then during the Second World War were widely used in the development of the "insecticide bombs". The propellants employed in U.K. aerosol formulations for which applications for carriage by sea have been submitted in the last 12 years may be divided into five groups: Aliphatic hydrocarbons (liquefied gases), chlorofluoroalkanes (volatile liquids and liquefied gases), chloroalkanes (volatile liquids), compressed gases (such as nitrogen, nitrous oxide and carbon dioxide), and mixed propellants (e.g. alkanes plus non-flammable components). *Fig. 3* and *Table 4* summarize relevant vapour pressure and toxicity data for these propellants.

FIG. 3



1 Propane
2 Propellant 12
3 65/35 propellants 12/11
4 *iso*Butane
5 50/50 Propellant 12/CH_2Cl_2
6 50/50 Propellants 12/11
7 *n*Butane
8 Propellant 114
9 Propellant 11
10 Methylene chloride
11 Chloroform
12 Methyl chloroform
13 Carbon tetrachloride
14 Trichlorethylene
15 Tetrachlorethylene

Aliphatic hydrocarbons

Liquefied butane and propane have been used because they are considerably cheaper than other propellants, being directly derived from crude oil distillation, but they are objectionable in that they are extremely flammable. Four insecticides, containing 25 to 27% butane were submitted in 1954-7 and were recommended for carriage under the conditions appertaining to flammable compressed gases. Alkane propellants were not then generally favoured but have since found a special use in a variety of three-phase systems, e.g. starch, polish and window cleaning sprays, wherein liquefied butane (between 2 and 10% of the total formulation) floats on a denser immiscible aqueous solution of the concentrate. Such a system will not release neat butane providing the container remains upright but if discharged in the inverted position, an extremely flammable spray is emitted. In the past three years, 24 products of this type have been examined for which the special closed beaker test described in the previous section was evolved. The testing of such formulations may be complicated by the presence of flammable solvents, which despite any water present, may render the spray significantly more hazardous.

A more recent development has been the introduction of dispensers fitted with a vapour phase valve, or tap, for multiphase systems. By courtesy of the Metal Box Co., a number of these dispensers containing trial formulations were provided for our examination. A small aperture (0·5 mm) in the valve housing is designed to admit some of the top (gaseous), as well as the lowest, phase, which then mix in the valve head. Such dispensers, fitted with a break-up actuator where necessary, may be used inverted, or indeed in any other position. Larger quantities of butane (say, 30 or 40%) can be included in formulations for these dispensers, thereby much reducing the risk of exhausting the propellant, leaving residual concentrate that would be wasteful and, if flammable, potentially dangerous. Despite the higher butane content, the spray emitted contains finely atomized water droplets that effectively suppress ignition, whether the dispenser is vertical or not. In the closed beaker test, a horizontal condensation front is formed between saturated butane and air which, when ignited, slowly sinks and the butane burns quietly (i.e. not explosively) at the interface. Thus, it would appear that the vapour phase valve offers significantly less danger were this type of formulation discharged in a poorly ventilated, confined space. However, it should be emphasized that such protection is not a relevant consideration for large-scale storage : a slow, vapour leakage would be rich in the most volatile component, in this case—butane.

Chlorofluoroalkanes

The development of these compounds in the 1930's for a number of

purposes by various manufacturers resulted in a chaotic nomenclature which has only recently been standardized. It may now be accepted that the designation of a specifically numbered propellant as *Freon* (duPont), *Arcton* (ICI), *Isceon* (Imperial Smelting), *Genetron* (Allied Chemicals) or *Algofrene* (Montecatini) will connote the same halogenated hydrocarbon. These gases and volatile liquids are regarded as chemically inert, non-flammable (flame quenching, in fact) and only slightly toxic ; they are, however, suffocating in heavy concentrations, as might arise, since they are considerably denser than air, in the well of a badly ventilated hold were the contents of a sufficient number of dispensers to be released. It has been shown[9] that a 10% concentration in air of propellant 11 is lethal to rats in 20–30 minutes. For proximity to living quarters, however, it is appropriate to consider the internationally recommended Maximum Allowance Concentration in air to be experienced during an 8-hour working day, which for propellants 11 and 12 is given as 1,000 ppm, i.e. 0·1% by volume or 5 mg/l. Considering a formulation containing 80% of mixed propellants 11 and 12, the MAC would be exceeded locally if the propellants of only one 12 fl. oz dispenser were completely to evaporate into an unventilated space of 48 cubic yards (e.g. a hold floor area of 18′ x 12′, to a depth of 6′). If 100 containers failed in the same space, a potentially lethal concentration would result.

The most widely used system supplying a pressure of about 3·1 atm at 21° comprises an equal mixture by weight of propellant 12 (dichlorodifluoromethane, a gas, bp. —29°) and propellant 11 (trichlorofluoromethane, a liquid, bp. 24°) ; cylinders with this mixture under pressure are readily available. It has been our experience that not only is the potential flammability of a spray reduced, or entirely quenched, by high proportions of this mixture but that also the presence of the higher boiling propellant 11 helps to suppress ignition of the residual liquid, when exposed in an open dish, until the latter has been warmed. Thus, it has been noted that certain hair lacquer formulations, containing substantial quantities of ethanol and relatively small amounts of propellant 12 (only), are significantly hazardous as judged by our performance tests. In other hair lacquers more recently examined, half of the ethanol has been replaced by propellant 11, whereby the pressure is maintained but the flammability is much reduced.

Other proportions of propellants 11 and 12 are less frequently employed but, recently, to meet the demand for higher pressure blends, some formulations have been submitted in which various amounts of another liquefiable gas, propellant 114, are mixed with propellant 12. Propellant 114, symmetrical dichlorotetrafluoroethane, bp. 3·5°, is intermediate in volatility between propellant 12 and 11. The pressures (in atmospheres) of the three propellants at 55° are 13·3, 5·0 and 2·7 (*Fig. 3*). Octafluorocyclobutane, propellant C.318, has been approved by the U.S. Food and Drugs Adminis-

tration as a pressurizing agent for foodstuffs. This perfluoroalkane, bp. –6°, has a vapour pressure (of 2·7 and 8·5 atm at 21° and 55° respectively), very similar to the commercial 50:50 mixture of propellants 11 and 12 at ambient temperature but increasing more steeply above this. It is non-toxic, non-flammable and exceptionally resistant to hydrolysis; duPont found[4] (p. 50) a rate of hydrolysis one twentieth that of propellant 12. It has been stated[10] that mixtures of the new propellant with nitrous oxide "will be immediately available", but thus far, no products containing this agent have been examined in our laboratory.

Chloroalkanes

Chlorinated hydrocarbons in general, and methylene chloride and *Chlorothene* (methyl chloroform) in particular, have been used in preference to flammable butane, for partial replacement of the more expensive chlorofluoroalkane propellants and serving simultaneously as cheaper solvents. However, the chloroalkanes are somewhat more toxic than the chlorofluoroalkanes, the hazard increasing in the order propellant 12, propellant 11, methylene chloride, *Chlorothene*, trichlorethylene, leading to chloroform and carbon tetrachloride. To date, we have only found *Chlorothene* in a few shoepolish formulations but methylene chloride is commonly used. Both the last mentioned solvents tend slowly to hydrolize in the presence of water, leading to corrosion of metal dispensers and ideally, therefore, should be reserved for anhydrous formulations. In practice, aqueous emulsions are frequently packed in internally lacquered tinplate dispensers.

Compressed gases

Concentrates pressurized by compressed gases suffer a constant loss of pressure as the product is dispensed. However, higher filling pressures may be permitted since the proportional increase in absolute pressure between (say) 20° and 55° is only about 20%, which is much less than that for a liquefied gas (2- to 3-fold). Advantage of this latter factor is taken in the boosting of a medium-pressure formulation (e.g., the large refill dispenser of a "mother and daughter" cosmetic pack) or the dispensing (through a suitable valve and cream-spout actuator) of toothpaste or haircream. In our experience, nitrogen has been used in both these ways; the (absolute) pressures recorded have not exceeded 8 atm at 21°. Carbon dioxide or nitrous oxide have been used to pressurize certain other products, particularly foodstuffs, in which they are partially soluble. The equilibrium, between gas under pressure and gas dissolved in the liquid phase, is disturbed when product is discharged, reducing thereby the headspace pressure. No question of toxicity or flammability arises with dispensers containing these propellants. The sole considerations are the ullage (and hence pressure) at

the maximum likely temperature, and any inherent hazard of the residual concentrate if the pack were inadequately pressurized.

Mixed propellants

It has been shown[11] that up to 25% by volume of propellant 12 may be replaced by propane or butane before a flammable mixture results; this constitutes a saving in both cost and weight to the formulator. Reed developed a medium pressure blend of propellants 12 and 11 and *iso*butane (45:45:10) which is said to be non-flammable[12] and, which was available in the U.S.A. in 1957[13]. A blend using larger amounts of the somewhat less volatile *n*butane (proportions 20:50:30) was examined by us in 1954, and recommended to be labelled as for "butane". More recently, we have noted that the presence in three products of 50% of a methylene chloride/trichlorethylene mixture failed to suppress the flammability due to 12% propane and 30% aromatic solvents. It was found that this mixture frequently caused failure of "O" seam containers stored at 55°; the maker subsequently submitted a less highly pressurized, non-flammable propellant system for his product.

Chloroalkanes have also been used as pressure diluent and complementary solvent in 4-phase systems. We have examined a number of household product dispensers, fitted with vapour phase valves, in which roughly equal amounts of butane, water and methylene chloride are employed. The spray of these formulations is not flammable, whilst in the closed beaker test, the vigour with which the vapour will burn depends largely upon the relative proportions of the three components and also whether the dispensers are shaken before being discharged.

Current research in the United States[12] has developed a high pressure blend containing dimethyl ether (15% by weight of liquid) and propellant 12. Having examined various proportions of these two gases in an apparatus similar to that employed by the U.S. Bureau of Mines, Scott *et al*[12] claim that a vapour mixture of composition 30:70 by volume (i.e. 15·6% by weight of liquid) is just below the lower explosive limit for all concentrations of this mixture in air. It is further stated that fractionation during slow leakage, giving rise to flammable "tail fractions" enriched in dimethyl ether (bp. —24°), can be avoided by replacement of propellant 12 by a 90:10 mixture of 12 and 11. For comparison, the vapour pressures of propellant 12 and dimethyl ether at 21° are 5·7 and 5·1 atm respectively. It is not expected that this propellant blend will be used in U.K. production in the near future. Scott has also described a blend containing vinyl chloride[14] and investigated[15] high, medium and low pressure blends using the hydrocarbons propane, *iso*- and *n*butane respectively. It is questionable whether any (commercially) significant mixture of propane and propellant 12 is likely to be non-flammable. The maximum tolerable amount of *iso*butane for a non-

flammable medium pressure blend was found to be 14% (by weight of liquids); fractionation lowers this value to 12%. Reed[13], it has already been noted, recommended 10% *iso*butane when the diluents are a 1:1 mixture of propellants 12 and 11. For a low pressure blend, Scott[15] examined *n*butane/propellant 114 mixtures and concluded that the butane content must not exceed 8·5% by weight, which, allowing for fractionation reduces to under 7%; in commercial practice, the resultant pressure would be too low. A blend used to pressurize perfumes contains *n*butane and propellants 12 and 114 in the proportions 11:9:80.

Protective Cap

All specifications require that the valve actuator button shall be adequately protected from accidental discharge by a cap or cover. Sweden cite an alternative threaded knob whilst for pyrethrin insecticides, the CPO[5] specify a cap of polyethylene conforming with Ministry of Defence Specification DEF 101. A cap may be considered unsatisfactory because it is too easily deformed or dislodged or if the clearance inside the cap, above the valve button, is too small.

Laboratory examination of the cap reveals the dimensions and apparent construction, and a subjective estimate is made of the ease of horizontal dislodgement under both a steady applied force and short, abrupt blows. The internal clearance above the button is measured and then a series of increasing loads is applied vertically to the cap, up to a maximum of 200 lb or until the valve is discharged. Similar tests are made on containers that have cooled following storage at 55°. The equivalent pressure required to operate the valve is calculated from the area of the cap to which the critical load is applied. The clearance will depend upon the type of valve, length and design of button and height of the crimped shoulder of the cup above the domed end of the case. A wide variety of protective caps are available.

Sturdy cylindrical *tinplate* caps, of 33 mm external diameter, fit snugly over the cup of the valve insert and normally effectively resist moderate horizontal and vertical pressure. These caps are usually about 19 mm tall, with a slightly domed end adding another 1 mm to the height; occasionally, poor internal clearance above the valve button renders the cap unsatisfactory. A wider (50 mm) cap, fabricated from 0·4 mm tinplate, which fits over the full shoulder of the dispenser, has been found to be too flexible and the valve button is inadequately protected; on objection, it was stated that this cap is only used for the "home market". A special applicator, with modified cap has been fitted to the dispensers of wood-worm preparations; a miniature tinplate cap (diameter about 24 mm) fits over the button but inside the valve cup, whilst through a slot in the cap protrudes a polyethylene delivery tube connected by a brass adapter to the valve and terminating in a brass jet

backed by a 25 mm diameter circular rubber shield. Following use, there is some dribbling from the delivery tube but this is not a hazard relevant to carriage or storage.

Plastics caps are particularly common. They are most frequently moulded from polyethylene ; cellulose ester caps are generally more rigid and less deformable under load but some have shown a tendency slowly to embrittle. Thus, when pressure was applied to a cellulose ester cap of a dispenser that had been stored for two years, the cap instantly shattered. High density polyethylene is also subject to environmental cracking with certain solvents, especially aromatic hydrocarbons. To minimize exposure to the vapour of these solvents, some polyethylene caps are vented, i.e. bearing two or more fine holes, which are (presumably) intended to permit evaporation of solvent spilt into the cup during use.

The majority of plastics caps are cylindrical, 31-33 mm internal diameter and usually 20-22 mm high. One series, available in both high density polyethylene and cellulose ester, which is particularly popular in the home-market, has generally been considered unsatisfactory for export unless special features of the inner packaging attenuate direct loading on the caps. The internal height is only 18 mm which for transport and storage purposes may be considered an inadequate clearance (less than 2 mm) above the valve button.* The basic cap design may be improved by a variety of integrally moulded features. Thus, resistance to a vertical load is assisted by fluting the sides and/or the provision of internal ribs, whilst adherence to the rim of the valve cup, normally achieved by an annular thickening of the cylinder wall moulding to form a "gripping ring" below the fluting, is improved by the presence of 3, 4 or 6 flanges. The cylindrical pattern is subject to further modification. Thus, polyethylene caps may be moulded in a conical frustum (half-barrel) shape. One such cap has an internal diameter of 33 mm, tapering to 24 mm, and is further supported by three substantial internal ribs ; this form achieves a better load resistance, albeit slightly increasing the ease of dislodgement. Another polyethylene example, recently submitted, has less to commend it. It is more flexible, has less taper (i.d's. of 33 and 26 mm) and little significant additional support is given by four slender moulded struts ; this cap will resist moderate loads when fitted to the (broader) 12 oz dispensers but tends to splay, thereby releasing the valve, when tested with the smaller (narrower) containers. The logical extension of this frustum trend is seen in a tough, hemispherical, cellulose ester cap with an equatorial grip-ring and 6 internal flanges. These caps are not easily dislodged and offer excellent resistance to applied loads. Unfortunately, a deceptively similar cap, made of thin polyethylene, is

*This design has since been modified by the manufacturers to give a satisfactory internal clearance.

available which dimples readily under load and the valve button is discharged. A number of dispensers have been fitted with an example of the contrary trend in style—a strong, thick, polyethylene, cover in the shape of a "pork-pie" hat ; this is one of the strongest plastics caps in our experience.

A specialized dispensing cap has been fitted to a herbicidal preparation. A 50 mm diameter, 12 mm maximum height, polyethylene, mushroom-shaped cover with six slender ribs, fits over the brass valve stem. From the middle of the top of the cover, a 25 mm extension leads to a fine metal jet, which in turn is protected by a 12 mm plastic stall. It was found that quite gentle vertical pressure on the shoulder of the cover was sufficient violently to force off the stall-cap and eject the flammable solvent. It has been recommended that for transportation a suitable cover be fitted to the valve and the dispensing caps packed separately.

Caps in a larger series, also generally moulded from polyethylene, are designed to fit the full width of standard 50 mm diameter dispensers. A variety of designs have been observed, all comprising flat-ended, smooth-wall cylinders of 48-52 mm internal diameter and heights between 27 and 32 mm. Resistance both to dislodgement and to a vertical load is furnished in three caps by a concentric cylindrical inner skirt of appropriate diameter to fit inside or outside the valve cup (one is described as a "Stack Cap") ; a fourth design has six rectangular ribs, a fifth includes four vertical pillars of outward-facing T-shaped cross-section which tangentially fit the valve cup rim and, finally, one has a stepped brim reaching down over the shoulder of the dispenser : this last design has been referred to as a "Top Hat" style.

Several types of *pilfer-proof cap* have been examined. One, of Norwegian origin, comprises a tough polyethylene cylinder, 30 mm internal diameter and finely fluted 15 mm sides, attached by 5 integrally moulded tabs to a larger collar (outside diameter 35 mm) ; this collar fits snugly about the valve cup. When submitted to steady pressures up to 130 psi., the upper, narrower portion of the cap sinks down onto the valve cup rim and under 160 psi. the button is momentarily discharged; the tabs, however, are still preserved intact. Neither will abrupt moderate blows with a hammer break them, but if the dispenser is allowed to fall from about 2′, cap downwards, on to a hard, wood-block floor, the union is severed. However, the cap is still retained *in situ* by the severed collar and continues effectively to serve as a satisfactory cover, resisting loading equivalent to 130 psi. Another tamper-proof closure, made in this country, consists of a moulded, ribbed, plastic dome retained by an aluminium foil overseal. This seal has to be cut and removed before the cap can be lifted. A similar overseal has been supplied with a slender, low-density polyethylene, vented cover (22 mm diameter base) designed to fit closely around the actuator button and inside the valve cup. Both these tamper-proof covers adequately resist applied loads of 200 lb.

Valve heads. All tinplate and aluminium containers, even the slim 1 oz size, that have been examined, incorporate a standard valve insert housed in a cup of 25 mm diameter. The plastics-covered glass dispensers normally have a specially designed valve head. For space sprays and most surface sprays, the typical 9 and 11 mm cylindrical polyethylene actuator buttons, with 0·5 mm orifices, are generally fitted ; occasionally a spatulate button occurs. Paint and other sprays of similar particle size (not "aerosols" in the strict definition) are dispensed through a coarser valve, with a breakup device in the button ; a wide angle orifice may be fitted or sometimes a special "Howitzer" style button. Containers for foam forming preparations, such as shaving creams, are fitted with so-called "cream spouts" with an external orifice of about 8 mm. An alternative actuator operates the valve by a disc-lever through which the foam passes to the "cream spout".

The valve head is inserted in a standard 25 mm stamped tinplate cup, fitted with a rubber grommet and crimped to the domed end of the case ; the crimped shoulder has an outside diameter of about 32 mm. Where a container has leaked during heat storage, on only one occasion has it been evident that the grommet had been displaced. Aluminium cups would be considered desirable for insertion in aluminium cases, to avoid electrolytic corrosion, but none has been observed. Inspection suggests that frequently the height of the top of a standard 11 mm actuator button above the domed shoulder is greater (about 23-24 mm) for 12 oz dispensers than (19-20 mm) for the 6 oz variety. Since a maker may often use the same caps for both sizes, it follows that the internal clearance above the button will be significantly less for the larger container, and may lead to the anomalous conclusion that a given cap is not satisfactory for all sizes of an apparently similarly constructed dispenser. The same anomaly arises with some paint dispensers, where the valve cup may have a taller boss. Another cause of failure adequately to resist an applied load, the splaying of the fluted walls of a polyethylene cap, is usually found with slim containers (e.g. the 35 mm diameter, 1 oz dispensers), or where the domed shoulder of the case slopes steeply away from the cup rim ; in such an event, a sturdy tinplate cap is the better fitting. Reference has already been made to a conical cap which splays more readily on the shoulders of the slender (up to 8 oz) dispensers.

Transport Restrictions

Applications for *carriage by sea* are scrutinized in the manner outlined in the preceding sections in order to assess the hazards that might be offered "to ship or crew" by the container and its contents. If for any reason the proposed packing is considered to furnish inadequate protection, modifications are suggested. Where possible, an application is related to a product of similar type for which the Minister of Transport's Standing Advisory

Committee has already approved a packing and/or one which has an established safety record. Existing precedents are observed in stowage restrictions which are based on experience of application of the Safety Rules. Labelling and Declaration are the least clearly defined aspects. Advice on questions of stowage and packing may be sought through the Ministry of Transport from their Marine Surveyors and, in the ultimate, any substantive doubt as to whether an existing provision can safely be relaxed is referred to the Standing Advisory Committee.

Occasionally, a product can be recommended as offering no significant hazard to ship or crew and may then be declared as "non-hazardous" (as, for example, an aqueous non-flammable emulsion pressurized by only 6% of propellant 12 or by an inert compressed gas). More often, such a packing can be recommended that enables a product to be described as "non-hazardous when packed as proposed", although it may be necessary to add certain provisions as to stowage. If the composition of the product is not sufficiently hazardous to warrant specific declaration under an appropriate entry in the "Blue Book"[1], (e.g. large quantities of Toxic—Section 4, or Flammable—Section 5, substances when the dispensers would have to be packed, stowed and labelled accordingly), the product might nevertheless be classified under Section 10 ("Other Dangerous Goods") of the "Blue Book", labelled as "Low Pressure Aerosol Dispensers" and stowed as specifically recommended. Recommendations for packaging, stowage and labelling are conveniently summarized according to the hazard concerned.

Unless the composition is regarded as completely non-hazardous a *general restriction* is suggested concerning stowage in the vicinity of strong acids (for tinplate containers), and also of strong alkalies (for aluminium containers). Plastics-covered glass dispensers are usually packed in outer wooden cases and, of course, recommended to be stowed away from external sources of heat.

Where one or more containers show significant evidence of *leakage or visible distortion* following 18 hours' storage at 55°, further samples, from different batches if possible, are sought and tested. Containers that burst open at the seam or persistently leak are not normally considered suitable for carriage through tropical conditions. If conveyance in temperate latitudes only (as defined above) is then sought, fresh samples are tested at 45°. Dispensers that have failed on heat storage may still be carried subject to consideration of the contents. If chlorofluoroalkane propellants constitute the principal hazard (cf. the comments on asphyxia and lethal concentrations in the section on propellants), storage "on deck only" in wooden outers, has been suggested. Where potentially more dangerous components are present, the risk to ship or crew associated even with "on deck" stowage must be evaluated.

Products pressurized by propane or butane are liable to release *flammable gases* if the dispensers are crushed or fail, or if the valves (excluding the vapour phase taps) are discharged with the dispenser in an inverted position. When large amounts of these hydrocarbons are present, or a mixture of moderate amounts of butane and readily flammable liquid(s), an A3 ("Inflammable Gas") label and stowage "on deck", using wooden outer cases, are usually recommended. When the amount of butane and the performance tests justify it, carriage "under deck, in a well-ventilated compartment" (usually "'tween deck") may be suggested. It sufficient water and/or (quenching) chloroalkanes are present, strong fibreboard outer cases ("under deck" only) may be allowed, whilst with suitable, strong, wooden outers, the A3 label may be waived and the dispensers simply declared under Section 10. In a number of household preparations, which comprise essentially an aqueous emulsion or suspension with small amounts of butane and no other flammable component, explosion of the vapour may not occur, although, at about the 5% level, the butane will burn non-violently notwithstanding the presence of 90% of water. For this reason, declaration under Section 10 will still be necessary but such dispensers may be packed in strong fibreboard or wooden cases, carried on or under deck and need not necessarily bear the A3 label.

Recommendations for other *flammable constituents* depend mainly on the results of performance tests but the composition of a product is taken into account. If there is a relatively large amount of class A or B flammable substances (i.e. normally possessing an Abel, closed cup, flash point (A) under 73° F or (B) from 73° to 150° F inclusive), and especially if little or no higher-boiling inert propellant (e.g. propellant 11) is included, then a declaration under Section 5 is considered. Certain paint and medicinal preparations may be allocated to their appropriate less restrictive entries in that Section. Formulations containing smaller quantities of flammable components, particularly where—as in space sprays—a large excess of chlorofluoroalkane is present, may, depending upon performance, be suggested for carriage under Section 10 or declared as "non-hazardous in the proposed packing". The Standing Advisory Committee has from time to time reiterated its view that a strong wooden outer case should be employed where a significant amount of class A flammable substance is present but that strong fibreboard outers, capable of withstanding likely overstowage, would suffice for components flashing only in the class B range. In this context, the steel, demountable railway containers carried on a train ferry are considered a satisfactory outer packing *per se*, provided that such "containers" only contain aerosol dispensers. Very small quantities of flammable components are ignored for the purpose of classification, although precise limits have not been defined.

Consideration is given to the relative *toxicity* and vapour pressure of the more volatile chloroalkanes, used as solvent and/or pressure diluent, and where the amount of such a component justifies this course, the provisions of the "Blue Book" for the carriage of the corresponding pure chemical is recommended. In line with the Standing Advisory Committee's recent recommendations, dispensers containing significant amounts of many of these toxic solvents may be carried in either wooden or strong fibreboard cases, providing these are considered capable of withstanding likely overstowage. If these solvents in quantity represent the only significant hazard, declaration may be made under Section 10, although if fibreboard cases are to be used, the affixing of a C—"Poison"—label normally is advised, and in any event, a stowage restriction relative to living quarters. There are certain additional recommendations appropriate to the carriage of carbon tetrachloride.

Continental restrictions relating to the transport of low pressure dispensers containing chloroalkanes have been summarized elsewhere[4]. In 1961, these solvents were not allowed in Swiss aerosol products, whilst poison labels were required in Norway and France if 25% and 30% (up to 8 oz containers), respectively, of methylene chloride were present; generally, formulations with more than 5% tri- or tetrachlorethylene or methylene chloride required "poison" labels.

It is unlikely that a domestic aerosol product would be marketed containing large quantities of highly *toxic ingredients*, but this aspect of the composition is considered. Usually it is possible to recommend relaxation of the special provisions of Section 4 (Poisonous Substances) for small quantities but certain stowage precautions may be relevant. Even these may be waived if it can be shown that the risk is purely a commercial one. Thus, whilst insecticides containing pyrethrins and their synergists are not regarded as hazardous, it is normally recommended that aerosol formulations containing DDT, BHC, dieldrin and related chlorinated tetracyclics, chlorinated camphenes and alkoxyethyl isocyanates should be stowed away from food and foodstuffs. A similar requirement suffices for small amounts of malathion but were preparations containing significant amounts of other, more toxic, organophosphates proposed, it is probable that more stringent precautions would be advocated. An insecticidal spray containing 0·5% DDVP dispersed in a hydrocarbon solvent has recently been registered in the U.S.A.[16]; this organophosphate, although an extremely potent inhibitor of cholinesterases, having a toxicity comparable with that of dieldrin, is rapidly hydrolyzed by moist air, leaving innocuous artefacts. Any proposals relating to aerosol dispensers for this material would have to be evaluated most carefully. Pharmaceutical and veterinary preparations, though not necessarily particularly toxic, are frequently recommended not to be stowed

near foodstuffs. Similarly, dispensers containing a product liable to be offensive if released, are restricted relative to living quarters and stowage of foodstuffs.

Where it has been shown, following the tests described, that a *protective cap is unsatisfactory*, it is usually recommended that strong dividers and/or layer pads be provided within the inner carton and, if the spray that would be discharged is especially hazardous, an outer wooden case be used. If a cap is found to be particularly unsuitable, it is suggested that alternative designs be considered.

For the carriage of aerosol dispensers by *Inland Mails*, the G.P.O. have their own regulations and approve suitable packings. It is in connection with *Overseas Mails* that the advice of this Laboratory is sought. Once a mail bag has been sealed, there can be no knowledge or indication of the potentially hazardous nature of the contents, nor can other than general stowage precautions for P.O. mails be taken. Whilst the number of dispensers carried in this way will, of necessity, be relatively small, there may be a possibility of a fire from leakage in a mail bag—and fire in a ship or aircraft can be a very much more serious matter than in terrestrial storage. In these circumstances, only the most innocuous formulations are likely to be accepted as anonymous freight.

The I.A.T.A. regulations for the *carriage by air* of "restricted articles" require classification of aerosol sprays according to the hazardous nature of the contents; in some cases of doubt as to the correct classification, products have been examined in this Laboratory and the Ministry of Aviation advised. The extremes of temperature (quoted earlier in this paper) anticipated in flight and in ground storage are not more extensive than those considered for carriage by sea.

In the unpressurized holds of some older types of cargo aircraft, and possibly some future jet transport, the pressure differential at 35,000′ would be about 0·75 atm, whilst in high flying aircraft that have been pressurized (to the equivalent of 8,000′), an accident resulting in explosive decompression would cause a fall in pressure of 0·5 atm. In practice, all containers for liquid "restricted articles" are required to withstand at least 1 atm and where aerosol products have been pressurized to 2·7 atm at 21° and/or 7·1 atm at 55°, the regulations for compressed gases shall apply[2] (p.68).

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Discussion

MR. C. BLOOM : Do you consider there to be any special hazards in handling dispensers which have been leak-tested at 55°C ? For example, what would be the effect of accidentally dropping a dispenser onto the floor as it is being withdrawn from the water bath ?

THE LECTURER : I have no specific experience on this point. I may make a few observations, however. Hydraulic tests on unfilled containers constitute purely internal pressure tests of the effectiveness of seams and crimping of the container. During hot storage testing, filled dispensers suffer two constraints : An internal pressure due to increase in vapour pressure of the contents and, additionally, heat may cause a weakening of the structure of built-up containers. We have found that when 12 oz (and larger) filled containers have been dropped on to an unyielding surface, from say 6 ft, there is usually some slight dimpling of the dished base though not usually complete inversion to the domed conformation. This dimpling may be due to the liquid contents having a separate momentum from that of the container. If motion of the liquid in the contrary direction is inhibited by the pressure in the overlying vapour space, raising that pressure by increasing the temperature presumably reduces hydraulic transmission of the shock, which would increase the strain on the base. This is quite conjectural because I have no direct experimental evidence of this.

DR. H. KÜBLER : Does the toxicity information given in *Table 4* refer to a 50% or a 100% lethal dose ? What is the source of this information ? What is the number of the patent dated 1889 which refers to ethyl chloride?

THE LECTURER: The data given are neither LD 50 nor LD 100; they are in fact 'Lethal Concentration' figures—mainly 'minimum LC,' except for chloroform and carbon tetrachloride for which LC 50 figures are quoted. The test animals were mice except for propellant 11, for which rats were employed. The figures were taken from Table II—'Lethal Concentrations of Gases, Vapours and Fumes in Respired Air' [Spector, W. S., Ed. *Handbook of Toxicology*, I (1956) (W. B. Saunders Co., Philadelphia and London)]. It should be noted that the figures cited in *Table 4* support Dyson's* comparison of methylene chloride with methyl chloroform. The patent referred to is Helbing & Pertsch, USP 628,463.

MR. A. HERZKA: What is the purpose of storage testing at 70°C?

THE LECTURER: This refers to a 1954 test result when an aluminium container failed due to leakage around the valve following 18 hours' storage at 70°C. The adoption of that test temperature in 1954 was, as explained above, in accord with the CPO practice. It should be noted that the CPO specification, which refers to dispensers to be stored and used by the Armed Forces overseas, still requires a (short-term) storage test at 70°C and, additionally, that unfilled containers, selected on a sample basis, should withstand a hydraulic pressure of 250 psig. This is an exceptional requirement.

MR. A. HERZKA: In testing for the flammability of the emitted spray, you apparently use four distances (50, 25, 5 and 1 cm), whereas in the C.S.M.A. Flame Projection test only one distance (6″ = approx. 15 cm) is specified. To which of the distances mentioned in your test do you attach most importance?

THE LECTURER: None. We consider all of them; one may get a false impression of the strength of flame projection if the test is made at one distance only; thus, as remarked above, ethanolic sprays show marked attenuation, that is reduction in strength with increasing distance of the flame from the dispenser valve.

MR. A. HERZKA: Will the two tests which you describe as approximating to the Closed Drum Test, and to the Modified Tagliabue test, be embodied in British Standard Specifications and the like, in due course? I must confess that the first of these two methods appears to be much more convenient than testing in a drum.

THE LECTURER: The DSIR is represented on the BSI Aerosol Dispenser Committee. I imagine that this Committee will consider *all* suitable methods for assessment of the flammability hazard of a pressurized formulation. No doubt, the relevant criteria will include simplicity, unambiguity, convenience of operation, reproducibility within and between laboratories. I should

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emphasise that the tests I have described have evolved over a number of years from simple *ad hoc* procedures used for Dangerous Goods classification purposes. I claim no special merit for them beyond that they are simple, convenient and reproducible.

MR. A. HERZKA : Can you describe a method, equally simple, to supersede the Open Drum Test ?

THE LECTURER : We have no corresponding test for propagation of flame in an enclosed space. However, as you have already remarked, we use four distances in our flame extension tests ; the 50 cm (roughly 20") test does give us some idea of propagation and also of variation in the flammability of the components if there should be any tendency for separation in the attenuated spray.

MR. P. MOXEY : Would you comment on any difference between the ambient temperature and the temperature of the contents of a dispenser?

THE LECTURER : I agree that the temperature of the exterior of metal containers exposed to the sun may be above the shaded air temperature ; however, only the contents in the gaseous phase will rapidly assume the exposed temperature and hence exert the corresponding vapour pressure but, fortunately for ullage calculations, the liquid contents will take an appreciable time to heat up and may never reach the skin temperature. Similar considerations apply to drums but there the question of elasticity and expansion of the drum alleviates to some extent the reduction in ullage as the external temperature rises.

MR. K. DIXON : The hot water testbath in production does not raise the temperature of the liquid contents to that of the bath. However, the pressure is very close to that when temperature equilibrium is reached.

With regard to liquid volume this is dealt with by allowing sufficient ullage in the can at the formulation stage.

THE LECTURER : I agree. Nevertheless, maximum vapour pressure and maximum liquid volume are two separate aspects. When related to likely maximum temperatures during storage, transportation and use, both aspects should be built into appropriate specifications.

MR. J. P. HALL : Could you enlarge on the internal protection found effective for the ovens ?

THE LECTURER : The precise procedure adopted will depend on the dimensions and design of oven employed. We fabricated a light alloy box of approximately 1 ft cube ; the lid is detachable and is restrained by four wing bolts. The walls do not exactly meet so that (hot) air may circulate through the box ; the base is raised above the oven floor by four small rubber feet.

The inside is slotted to take a number of light alloy partitions which restrict possible movement of glass beakers which have been fitted individually to each pressurized dispenser under test. It is important to allow free circulation of hot air within the oven and adequate time for the liquid contents of the dispensers to reach the test temperature. Further details would willingly be supplied if required.

MR. E. K. CLARKE : I would recommend the use of gloves and face shield when handling hot aerosol containers, and indeed would take care when handling cool containers that had been heated to 55°C.

THE LECTURER: In general, these precautions are wise. However, in the specific context of our oven test, the hazard is minimized by leaving the dispensers within the protective metal case for about 30 minutes before removal, either to complete their cooling prior to examination, or if the vapour pressure at elevated temperature (usually 55°C) is to be rechecked, for transfer to a screened water bath.

MR. E. K. CLARKE : You quote a test of flammability in a dish as being "more searching than the U.S. modified Tagliabue open cup test". If the flammability is "masked," why is it necessary to consider it, and what reason is there for having a more searching test.

THE LECTURER : In general, apparatus for the determination of flashpoint are designed to establish the lowest temperature at which a flammable vapour is evolved from a product as a whole. The Abel apparatus has a "closed cup" which tends to concentrate the vapour(s) evolved and gives consistently lower flashpoint values than the Tagliabue "open cup" equipment. This is well recognized in, for example, the IATA definition of a "flammable liquid" for which the temperatures 73°F in a closed cup tester, and 80°F in an open cup tester are equated. In both these, and related flashpoint methods, the actual apparatus may be considered an arbitrary design but the procedure is closely standardized and reproducible within narrow limits. During the course of our *open dish* test for combustibility, the product is allowed first to warm to room temperature and is then gradually heated. Under these conditions, progressively less volatile components have a much greater opportunity to evaporate than is possible in, for example, the equipment of formal apparatus for the determination of flashpoint. It is contended that such progressive evaporation bears more relation to conditions likely to obtain were the contents to leak from a container that had suffered structural failure or had been crushed. Nevertheless, practical allowance is made in our tests for the "masking" influence of any flame suppressant components present, on the volatility of which, relative to that of flammable component(s), the resultant combustibility will depend.

MR. D. ASDELL : I hope that when standards are being drawn up both within the cosmetic industry and/or within the aerosol industry, as far as possible they should cover the specific requirements of the test and not the method by which the test should be carried out. This is particularly relevant to the testing of aerosols. The draft British standard would read "that the container should be immersed for a specific period in a water bath of a specific temperature." I feel that this should mean that the dispenser be tested for a given period of time at a given temperature (or even the headspace at a given temperature) so that the pressure within the dispenser reaches a given figure and no leak or bursting should occur. It is particularly important that this type of specification be produced, otherwise the advancement of the industry could well be limited to one testing procedure, while everybody hopes that with the appropriate attention to development the forms of testing which are most economic should be used.

The majority of the explosive gases or vapours involved in the aerosol industry fall within those specified as Group II by British Standard 229:1959, and I believe that the use of aluminium is specifically excluded. Could the lecturer therefore explain why the use of aluminium aerosols can be accepted ?

THE LECTURER : In general, when a specification quotes a desired result, it is customary to cite an approved means of establishing that result. Such a procedure would usually be regarded as a referee method, whilst more convenient local methods can be, and frequently are, used to ascertain compliance with the specification—provided that it has first been established that the same result will be obtained by either method. In case of dispute, the reference method should be used. With regard to the example cited, I agree that the desired object should be stated ; if there is any doubt that a suggested method is unlikely to establish this object, then such evidence should be submitted to the relevant BS committee and other test procedures considered. Equally, I agree that the committee should take into consideration all suitable methods in arriving at a decision. In any event, British and other national standards are subject to periodic revision and the appropriate committees are reactivated.

BS 229:1959 refers to enclosures for electrical apparatus in the presence of flammable gases and vapours in air ; the study of gaseous reactions at metal and other surfaces is the province of the Safety in Mines Research Establishment, Buxton, of which work I have no personal experience. Such reactions are not necessarily relevant to conditions obtaining inside a metal container where the presence of air has been deliberately excluded.

SOME FACTORS RELATING TO THE CHOICE OF PERFUMES FOR PRESSURIZED PRODUCTS

R. E. ECKTON, M.A.*

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

The average consumer is rapidly becoming more odour-conscious and effective perfuming is one of the most important aspects of sales appeal.

Since perfumes are complex chemical mixtures, they are capable of entering into a variety of reactions in aerosol systems, and other factors not previously encountered have to be taken into account.

It is essential, therefore, that perfumes for aerosols are compounded specifically and that they are thoroughly tested under proposed conditions of use.

THE IMPORTANCE of odour in toilet preparations and household products of all types is now very clearly recognised. Effective perfuming or reodorising represents a major aspect of sales appeal. Exploitation of this is producing an increasingly odour-conscious public ; this trend goes forward hand in hand with our ability, by virtue of the production of new materials and accumulated experience, to meet the technical and economic requirements of perfuming an ever-widening range of products.

Aerosol products (which in this paper are taken to include wet sprays, foams, etc.) are expected to measure up to the same standards. The greater convenience in use of push-button packaging does not compensate for any inferiority in other respects.

Perfume compounds are complex mixtures from both natural and synthetic sources of organic chemicals, including alcohols, esters, aldehydes, ketones, acetals, lactones, ethers, hydrocarbons, acids, phenols, etc. It is hardly surprising, therefore, that many new problems have arisen in the application of these materials to aerosol systems. So many writers have described their experiences and contributed to our progress in this field that it is possible to draw attention only to some[1-5].

Thus, when producing or selecting a perfume for an aerosol, it is necessary to give careful consideration to many factors affecting performance and stability ; some of these are involved in the perfuming of non-pressurized products, others are peculiar to the aerosol.

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Aestheticism

The first desirable requirement is for the odour of the product to be acceptable immediately on release from the container. This involves adequate masking of the odour of the propellants, solvents or other ingredients.

DiGiacomo[6] has drawn attention to the way in which the perfume in certain aerosol products is presented to the nose in entirety rather than progressively from top note onwards as with conventional products. He also pointed out the effect of particle size, which depends on internal pressure and valve characteristics.

The perfume should be evanescent or persistent, according to the product, and must continue to mask any residual odour of the medium. No staleness or unpleasant effect as a result of successive applications should develop.

Irritation

This factor is always weighed seriously in the practice of perfumery but there are additional considerations in the case of perfumes for aerosols, especially where fine sprays are involved. New situations are created and unexpected effects of irritation of the nasal and other membranes can arise. The case of benzyl benzoate which, although widely used in dermatological preparations, gives rise to sternutatory effects in some aerosols illustrates this point[6].

Solubility

In most conventional products, incomplete solubility of perfume would most certainly be undesirable, as it would be uneconomical and could result in an unsightly appearance of the preparation, but in the case of pressurized products it can be responsible also for malfunctioning of the dispenser owing to valve blockage.

The normally used halogenated hydrocarbon propellants are not the best of solvents for many perfumery materials. In some aerosol formulations, other ingredients such as alcohols and glycols exert a favourable influence, whereas hydrocarbons and water for example, can aggravate the situation. Insolubility is not always obvious at once ; precipitation of gummy or other residues can be progressive as the system reaches equilibrium. It is possible to process some natural products and to develop special synthetics with solubility in mind, so that the restrictions are not an embarrassing limitation.

Corrosion and other action on containers and components

Apart from the action of certain organic acids and alcohols on some metals, the part played by perfumery materials in container corrosion is incompletely understood. It is certain, however, that their presence in a given system can exert an influence on the degree of corrosion resulting.

They may be acting as catalysts or inhibitors, and their own action may be influenced by another ingredient of the product[7]. Equally, the effect of perfumes on plastic and rubber components cannot be ignored.

Chemical Compatibility

Familiar reactions of perfumes with products under normal circumstances may be modified under aerosol conditions. Proneness to oxidation and the effects of light, for example, may be reduced, but on the other hand certain perfumes may react with propellants or with the metallic, and other, products of interactions taking place in the aerosol.

The commonly used propellants are comparatively stable, the most reactive being trichlorofluoromethane. If water is present, the latter can be hydrolysed catalytically with the liberation of acid. Furthermore, it has been claimed that under certain conditions ethyl alcohol will react with this propellant[8,9]. A variety of isomerisations, cyclisations, etc., of perfumery materials can take place when the pH is thus reduced. Witjens[10] has shown how ethyl alcohol is dehydrogenated to acetaldehyde under the influence of acid and metal or metal halides, especially if water and oxygen are present. The acetaldehyde would be capable of entering into a variety of reactions with perfumery chemicals under these conditions. It is even conceivable that certain perfume ingredients could facilitate the primary reactions, for example by acting as a free radical initiator or a hydrogen acceptor. The ideal is to formulate and pack aerosol products in such a way that the drastic initial changes are avoided. In this case, the questions to be considered when selecting a perfume are less complex. However, as a compromise is often the nearest approach to the ideal, the perfumery chemist must take into account all relevant factors when making recommendations if odour changes, discolouration and formation of insoluble residues are to be minimised.

Physical Compatibility

The effects of perfumes on viscosity and emulsion stability of some non-pressurized products are well recognised. They are equally important in the field of aerosols. Detrimental effects could be the precipitation of wax from pressurized polish or the poor foaming characteristics of a shaving cream.

Testing

It follows that adequate testing of perfumes in pressurized products is essential. Countless evaluations of the behaviour of individual ingredients in various aerosol systems have been made[11,12], and continue to be carried out. The results of these are extremely valuable from both the practical and theoretical aspects but they do not obviate the necessity for testing

finished compounds, in which each ingredient can modify the behaviour of others. For example, in the first of the papers just cited[11], the conclusion is reached that the odour of hydroxycitronellal is changed in a typical aerosol cologne, but we know that this chemical is used with great satisfaction in many perfume compounds for this application. Similarly, solubility determinations on single ingredients may have no bearing on their behaviour in particular concentrations in compounds. In the second paper[12], it is shown that coumarin is insoluble at 1% in propellants, but this by no means precludes the effective use of this material in practice. Nothing can replace the adequate testing of a perfume compound in the precise formulation and pack under normal storage conditions. However, where time is limited, accelerated tests at elevated temperatures can be of service if interpreted on the basis of considerable previous experience.

A typical testing procedure in the case of a perfumed pressure pack would involve the preparation of twelve packs exactly as proposed for marketing. Six would be placed in the incubator at 130°F, and six stored on the shelf at room temperature. At suitable intervals covering a period of one year, one shelf container and one container from the incubator would be examined for odour change, for corrosive effects on all the internal metallic parts and for swelling effects on the plastic components, also for any evidence of deposition of insoluble matter and for changes in the colour, pH, etc., of the solution. Odour comparisons would be made with control unpressurized solutions kept under the same conditions and at appropriate intervals with freshly prepared pressure packs.

In order to supplement these generalisations, some specific points of importance in the perfuming of individual groups of aerosol products are described below.

Air Fresheners

The function of an aerosol air freshener is to eliminate undesirable odours from the atmosphere to be treated.

Some of the theories of space odour removal have been described in detail by Gee[13] and Johnsen[14]. In brief, this can be achieved by masking the unpleasant odour with one which is more acceptable, by blending another odour with it to give a neutral effect, by temporarily anaesthetizing the sense of smell, or by chemical combination with the malodorous molecules to give less offensive complexes.

The part played by perfumes is obviously very important. The design of perfume compounds to participate in these various mechanisms of odour removal, including the entering into polymerisation and condensation reactions with a variety of active groupings, is a subject of constant research and experiment. Systems have been designed for assessing the effect of

potential ingredients on a variety of odorous materials under controlled conditions[13,15]. Unfortunately, the spaces into which air fresheners are sprayed are not laboratories into which carefully dosed amounts of specific malodours have been released. The latter are complex and infinitely variable in chemical nature, and it is impossible in practice to adjust the ratio of material sprayed. Thus, whilst the theoretical background and fundamental research are taken very much into account, perfume compounds recommended are to a certain extent empirical in nature and result from practical testing under conditions of use.

In cases where a non-perfumery chemical such as lauryl methacrylate is included in the formulation specifically to react with odorous materials in the air, it is important not only that the perfume does not react with it in the dispenser but that it does not compete for it in the atmosphere after spraying. This calls for careful co-operation between perfumery supplier and aerosol producer.

Air fresheners are by no means used only where a definite malodour is to be removed, but very often to give a pleasing odour and restore agreeable conditions in rooms where there is a tendency to staleness. Thus, odour preferences cover a very wide range, with the emphasis usually on freshness. It has been stated that certain fragrances are able to exert a refreshing action by virtue of their ability to counteract the vasoconstrictive effects of stale air on the body[14]. Freshness is interpreted variously in the form of lemon, pine, lavender, cologne, etc., but this is being modified as the demand for greater suavity makes itself felt. Light bouquets with a greenness reminiscent of the countryside are examples of progressive requirements.

An increasingly important branch of aerosol air fresheners is that aimed at reducing the microbiological population of the atmosphere. The need for compatibility of perfumes with the active ingredients is self evident, and factors arising from the tendency to introduce a higher water content with efficiency in mind justifiably deserve assessment.

Insecticides

Masking ability for the solvents and active ingredients, possible reaction with the latter and solubility, are points which deserve special review with respect to perfumes for insecticides. Since the solvents utilised are predominantly hydrocarbon in nature, solubility of perfumes is often quite unsatisfactory, and it is necessary to formulate them specifically with this aspect in mind.

Furthermore, many active insecticidal ingredients have a very marked unpleasant odour, which is augmented by that of certain solvents. These must be masked efficiently and economically to give as pleasing and appropriate a reodorisation as possible[16].

A suspicion that perfume compounds could adversely affect the insecticidal power of pyrethrum based insecticides appeared in the form of a public statement in 1959[17]. A survey made at that time concluded that there appeared "to be little or no documented foundation for any theory that perfumes destroy pyrethrins". Subsequently, a careful investigation reported by Pickthall *et al*[18] involving typical selections from the various chemical groups of perfumery materials, was unable to detect any significant reduction in pyrethrin potency attributable to them. Furthermore, certain materials, for example acetophenone and diphenyl methane, commonly used in perfumery have been shown to possess synergistic activity with respect to pyrethrins[19].

Our own experience confirms the view that perfume compounds do not represent a hazard in so far as reduction of insecticidal effect is concerned.

A specific requirement of perfumes for mothicides, which are sprayed directly on to fabrics, is that they should not promote staining.

Perfumes, Colognes and Toilet Waters

These consist essentially of a solution of the perfume compound in alcohol with or without a certain proportion of water, pressurized with either dichlorodifluoromethane or dichlorotetrafluoroethane, or a mixture of both. The possibilities of the complex reactions involving propellant, alcohol and water described earlier, taking place are thus greatly reduced.

The containers are normally either plastic-coated glass, internally protected aluminium, or stainless steel. The presence of water reduces the hazard of reaction between alcohol and exposed aluminium. DiGiacomo[20] has described the possible need for special cleaning in the case of stainless steel.

Perfume solutions should be chilled and filtered prior to pressurization by the methods utilised for traditional products. This procedure, allied to the fact that alcohol is an excellent cosolvent in the system, reduces very significantly the limitations arising from inadequate solubility after pressurization. With pressurized perfume presentations of this type, the principal effect comes from the alcoholic solution deposited on the wearer, so that provided there has been no undesirable change within the pack, it is the same as that from the corresponding unpressurized product. There is, however, some impression received from the "mist" when the product is being sprayed, especially with the drier sprays, so that the points mentioned earlier regarding impact on the olfactory receptors should by no means be overlooked. In this field, where olfactory quality is rightly expected to be of the highest, the presence of slight unanticipated impurities in the perfumery ingredients and alcohol used can be seriously detrimental, as their effect may be magnified disproportionately.

Where plastic-covered glass containers are utilised, the discolouring effect of light on certain perfume solutions should not be overlooked.

Hair Lacquers

The original products were based on shellac but, in view of various stability difficulties with the latter, most current formulations consist essentially of polyvinylpyrrolidone or associated co-polymers, dissolved in anhydrous alcohol with appropriate plasticizers, and pressurized with either dichlorodifluoromethane or a mixture of the latter with trichlorofluoromethane The products are usually packed in plain tinplate containers.

The possibilities of perfume breakdown under these conditions are considerable, and extreme care is needed in their selection and testing. It has been claimed[21] that the replacement of normal trichlorofluoromethane with a grade containing 0.3% nitromethane prevents degradation in hair lacquers and that in its absence 60% of packs develop objectionable odours within two months. Our own experiences by no means support the latter statement, where the lacquers are correctly filled and perfumed, and I am certain that many manufacturers will be of the same opinion. However, further experience may prove that the use of the stabilised propellant will reduce the possible hazards and facilitate the development of a wider range of suitable perfumes.

The predominant tendency originally was to use only sufficient perfume in hair lacquers to mask the initial and residual odour of the solvent/polymer solutions. The current trend, based on the realisation that the hair is an exceptionally good perfume absorbent, is towards distinctly positive odorisation especially where the hair lacquer is part of a range of toiletries. Such perfumes must remain pleasing throughout their life on the hair and must not develop stale or cloying effects in the residual stages.

Some perfumery materials form complexes with polyvinylpyrrolidone, unbalancing their effect. The plasticizing properties also must be considered carefully ; results have been reported on the reduction of film stiffness caused by certain perfumes, and a method of compensation has been described[22].

Whilst hair lacquers are essentially surface sprays, the user obtains a definite impression from the spray in the air and this must not be overlooked when an assessment is being made.

Foam Products

Whilst predominantly shaving creams, these include also hand creams, shampoos, cologne foams, etc. The propellant, normally dichlorodifluoromethane with or without dichlorotetrafluoroethane, is emulsified in the perfumed product and expels it as a viscous foam. Thus, the effects of atomisation do not have to be considered. Prior experience of the behaviour

of perfumes in non-pressurized creams and soaps is relevant when supplemented by careful assessment of the effects of propellants and metallic contamination. Discolouration particularly is to be avoided in order to retain the very pleasing aspect of a pure white foam. Some perfumes affect viscosity, and stability, in emulsions or detract from foaming power.

Personal Deodorants

The pressure pack is an ideal method of applying these preparations and is assisting in their establishment as toiletries with an accepted place in the hygienic routine.

The most popular products are based on *G–11*, which prevents the bacterial decay of perspiration, and in this way prevents body odours. *G–11* freely forms solutions in alcohol which, with the addition of perfume and a small proportion of a non-volatile solvent, followed by pressurization, yield very successful products.

In addition to the solubility, corrosion and compatibility aspects, we must consider here specifically the presence of *G–11*, and the known effects of perspiration on certain perfumery materials.

The perfume must cover the initial solvent odour from the spray, giving a light and revitalising effect. Whilst colognes and lighter bouquets remain popular with males, in the case of females there is a trend similar to that described for hair lacquers. The perfume in deodorants is increasingly looked upon as playing an important role in a matching range or as an individual adornment.

Sunscreen Products

With the advent of newer active ingredients, such as derivatives of 4-methoxycinnamic acid[23], possible reactivity is no longer an additional complication in the selection of perfumes. Apart from the obvious factors, we must bear in mind that sunscreening products are applied to large areas of the body which are then exposed to sunlight. The perfume must neither be too overpowering under these conditions nor contain ingredients which, by the influence of sunlight, are known to exert an adverse dermatological effect.

Household Products

This is a growing miscellaneous field, including starches, for which perfumes non-discolouring on ironing are required, polishes where the emulsion stability may be critical, spot removers with a solvent odour problem, etc. Masking compounds or positive reodorants are to an increasing extent proving themselves as definite factors in sales appeal.

Water-based Space Sprays

As a commercial proposition, these are comparatively new. The ideal perfume will neither aggravate the difficult corrosion situation, nor influence adversely the emulsion stability. Furthermore, it will be capable of diffusing with sufficient strength from the sprayed product in spite of the opposing influence of larger particle size and the restraining effect of water and surface active agents.

Conclusions

The varied problems associated with the perfuming of aerosols can be overcome and almost all aerosol manufacturers are now fully acquainted with the inescapable advantages of permitting perfume suppliers to co-operate with them as closely as possible. It is also being realised progressively that a too stringent cost allocation for perfumes is at most of short term advantage. The average consumer becomes ever more critical where odour is involved and the extra sales appeal of a product which is perfumed or reodorised in an effective, pleasing and reproducible manner is constantly making itself manifest.

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Discussion

Dr. W. Mitchell : "Exploitation of perfuming of consumer products is producing an increasingly odour-conscious public." This statement can have at least two meanings. In my opinion, the second, and apparently ambiguous, one is also true in that a section of the public is being forced increasingly to become conscious of odours that it neither likes nor wants ! This section of the public may be in the minority ; but that is not to say that it is the least discerning section—probably the reverse applies.

I think these circumstances arise because in recent years there has been an increasing tendency to add perfumes to all sorts of products whether or not their inherent odours are unpleasant ; and, furthermore, to add too much of such perfumes. Setting aside, for the moment, your professional and business interests as a perfumer, would you give your candid opinion on the theses that

(a) there is no real benefit to the consumer in the perfuming of products the intrinsic odours of which are not unpleasant, and

(b) that the intensity of perfuming of many consumer products today is too great.

The Lecturer : You emphasise the precise point which I am making—that the public are being made increasingly odour conscious because the potential of effective perfuming as a sales factor is realised. I have sufficient faith in the discriminating powers of the consumer to expect that he or she will not continue to purchase products with odours neither liked nor wanted, if better accepted alternatives are available.

As far as benefit is concerned, it depends what you mean. There are many consumer products with intrinsic odours which are not unpleasant. Toilet soap, many cosmetic creams, powders, bath cubes—for example. The perfuming of these was a natural cultural evolution, and it would be difficult to imagine the acceptance of such products without added perfumes.

Intensity of perfumes is a factor which is part of suitability. By effective perfuming, I intend that concentration and appropriateness should be taken into account. Some products are ineffectively perfumed by virtue not of excessive odour intensity but of incorrect choice of odour for the end use. Many experiments have shown that very skilfully perfumed products (silk stockings—for example) have been chosen repeatedly as better than untreated specimens, although the buyer was not conscious of the odour, another example of appropriate balance of odour concentration and type.

Thus, I think that we are in agreement, if you mean what I think you mean !

DR. W. MITCHELL : As some present here may recall, I was the author of the "public statement" about the adverse effect of certain perfume materials on pyrethrins. The lecturer is satisfied that the warning is groundless, but it was made by one with the advantage of wide experience not only with perfume materials but also with pyrethrum. Of course, a great many perfume materials do not have any effect on the pyrethrins, and if one is lucky enough to avoid using them, all will be well. As stated by the lecturer, acetophenone and diphenylmethane are two of these ; and they do also have a limited synergistic effect on the pyrethrins, though they are not in the same high class of activity as the two synergists, Bucarpolate and piperonyl butoxide, normally used in this country.

However, there are some perfume components that do have an adverse effect on the active principles of pyrethrum, though for obvious commercial reasons I am not permitted to name them. However, we have sounded the warning note. If others care to ignore it, or to prove to their own satisfaction that the danger does not exist—well, that is their affair. But the facts will not be altered !

THE LECTURER : I should like to say that no discourtesy was intended to you in respect of the "public statement". I was entirely unaware of its ultimate origin.

We should be very unwise to disregard the views of someone so widely experienced as Dr. Mitchell. We agree with him that certain concentrated chemicals do have the adverse effect described but our extensive experience with the types of perfume compounds which would be offered for use in insecticides, has led us to the conclusion that no real practical hazard exists.

MR. J. PICKTHALL : A few years ago we published results[18] of tests on 13 perfumery chemicals in insect control formulations containing pyrethrums. These were tested in the presence and absence of the synergist piperonyl butoxide by topical application of micro doses to normal house flies. Of the compounds tested phenylacetaldehyde had a slightly detrimental effect on the pyrethrum potency. As pointed out in the paper, phenylacetaldehyde is an unlikely ingredient in an aerosol perfume. The tests involved employed 0.5% of the individual ingredient which greatly exceeds the amount which would appear in a compound perfume.

An extension of this work was made by testing a bouquet made up of a number of synthetic chemicals, essential oils and isolates. Tests were made on a synergised pyrethrum mixture with and without perfume, sprayed from an aerosol in a 1,000 cu. ft. chamber. The perfumed samples revealed no reduction of potency.

MR. B. H. LANGLEY : Whilst not wishing to take part in the epic struggle between Dr. Mitchell and Mr. Pickthall, I feel (since reference is made by

the lecturer in his paper to a patent with which my company is concerned) that I should inform those present that as the result of tests with a wide range of aromatic (perfumery) chemicals it was found that many had activating and synergistic properties in relation to pyrethrins, and I would therefore incline towards Mr. Pickthall's views rather than those of Dr. Mitchell.

MR. A. HERZKA : Could you please explain the reason for carrying out accelerated storage tests at 130°F. We normally carry out accelerated storage tests at 95°F, and I believe that this practice is fairly general throughout the industry in this country. There have been occasions in the past, where a satisfactory behaviour at 130°F was no criterion for subsequent performance in actual use. Likewise, failure at 130°F does not necessarily imply failure at room temperature. We have even been criticised for adverse comments on perfumes after 8 months' storage at 95°F, the comment being that "the probability of a pressure pack being so stored for any length of time in the United Kingdom is extremely unlikely, if not completely so."

THE LECTURER : The procedure mentioned in my paper was a very abbreviated indication of the general methods adopted. We ourselves endeavour to choose a testing system which is appropriate to the objectives in view. Tests at 95°F are not seriously accelerated and we use this temperature, alongside room conditions, as a measure of what happens under these conditions, not to forecast what might occur under other conditions. It is quite correct that occasionally a formulation which survives accelerated tests at 130°F does not emerge with equal success from a year's room temperature storage. But, as you have reported, the same applies to tests at 95°F. There is no safe substitute for actual tests under expected conditions but our experience shows that, in cases where the results of previous similar work are available, a fairly accurate forecast can be made on the basis of tests at 130°F and room temperature for one to two months. In fact, the temperature of 55°C (131°F) is mentioned as a very useful guide in Herzka, A. and Pickthall, J. *Pressurized Packaging* (*Aerosols*) 2nd Edition 196 (1961) (Butterworths, London).

MR. J. PICKTHALL : Whilst it is quite true to say that an accelerated test is not a guarantee of ultimate success, nevertheless, such tests are extremely valuable, especially in development work. We prefer 130°F to 95°F simply because the test period is correspondingly shorter. We have found that one month at 130°F indicates the probable results equivalent to one year or more at normal temperature. In development work a product (particularly a perfume) which is degraded at 55°C after one month can be regarded as unsuitable. Naturally there is a possibility of rejecting a product which would in fact have survived twelve months at normal temperature but such cases are few and far between. On the other hand, if a product does survive

this rather drastic test then one can be pretty certain that it will be satisfactory over a long period of time at normal temperature. In our opinion, the advantages of the higher temperature greatly outweigh the disadvantages.

MR. S. J. BUSH : Is there any evidence that the irritant effect of sensitisers is increased when used in pressurized formulations?

THE LECTURER : Unexpected nasal effects have already been referred to. We have no evidence that the effects on skin are different by virtue of application from pressure packs.

MR. J. PICKTHALL : There seems no reason to suppose that irritation properties in a perfume would be increased when sprayed from pressure pack. Although the perfume may leave the aerosol in the from of droplets it meets the skin as a continuous film, and would perform in the same manner as an alcoholic solution applied from a normal container.

MR. S. J. BUSH : You mention odour deterioration due to interaction between PVP and perfume components. Have you encountered similar problems with other resins used in hair lacquers?

THE LECTURER : Our most extensive work has been carried out with PVP because this has been the most widely used polymer, but we have tests in progress on other materials. It is quite possible that similar effects will reveal themselves.

MR. G. F. PHILLIPS : What containers are used for the testing of perfumed aerosols for 1 month at 55°C ?

THE LECTURER : Many types, but most of our tests have been carried out with tinplate containers of normal design. I expect that you are interested in the leakage aspects, and we do experience some trouble in this respect. Tests affected must be discontinued but at least we learn something even from these.

MR. J. PICKTHALL : It is not possible to nominate a universal container for these tests. The perfume must be tested in the product itself, packed in the actual container envisaged for final sale.

AEROSOL PROPELLANTS

P. DYSON, B.A., B.Sc.*

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

The major properties, advantages and disadvantages of the established and the lesser used propellants are reviewed. Some detail is also given of work done on the thermal decomposition of halocarbons, which has a bearing on their use in aerosols.

INTRODUCTION

MUCH OF THE information in this paper is well-known ; the object has been to collect it into one place for easy reference. In addition, it is hoped that the paper may put into perspective some of the pros and cons that have often been brandished recklessly by the protagonists of one or other class of propellant. Vinyl chloride has anaesthetic properties, but not at concentrations remotely involved with its use of aerosols. The chloro- and chlorofluorocarbons can produce highly toxic products on decomposition in naked flames and on red hot surfaces, but it is virtually impossible by using an aerosol to create conditions where this would present a hazard to the user. Although it is my personal opinion that the uncontrolled use of flammable propellants could do nothing but irreparable harm to the industry, I feel just as strongly that there is no logical case whatever for a complete ban on the use of a flammable gas as a constituent of an aerosol.

Commercial aerosols were first produced in the U.S.A. in 1946, and in Europe and elsewhere from about 1951. Today, some 1,300 million containers are being packed every year and there is no indication, even in the U.S.A., that the market is becoming saturated. Hair sprays have been the best seller in the North American market for some years ; in the last year for which figures were published, 1961, some 150 million units accounted for nearly 20% of American aerosol production. In the same year, cosmetics as a class–hair sprays, shaving creams, colognes, perfumes and other personal products–comprised about one-third of U.S.A. aerosols, and a similar pattern is rapidly developing in Europe.

The majority of the world's aerosols contain chlorofluorocarbons and the safe properties and high standard of purity of these propellants have had much to do with the public acceptance of aerosols as safe and efficient commodities. Indeed, when the pioneers of aerosols chose the chlorofluorocarbons as propellants, they did so only after considering the properties of many other liquefied gases ; they decided that they alone had properties approaching closely to those of the ideal propellant.

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However, in such a progressive and competitive industry, attention will always be directed to the use of alternative propellants and diluents, either for technical reasons or to reduce the cost of the propellant element in aerosols.

Liquefied Gas Systems

A liquefied (or liquefiable) gas is defined officially in the United Kingdom as one which has a boiling point below 30°C but a more liberal description is "a gas which is gaseous at ordinary temperature but can readily be liquefied by the application of pressure". Thus a single liquefied gas in a closed container exerts a pressure which depends only on temperature and is independent of the quantity of liquid present. A mixture of two liquefied gases exerts a pressure intermediate between the pressures of the two components at any temperature. For "ideal" systems, Raoult's Law defines the total pressure of such mixtures as :—

$$P = m_1 p_1 + m_2 p_2$$

where m_1 and m_2 are the mole fractions of the two components p_1 and p_2 are the vapour pressures of the two components at the temperature considered.

Mixtures of the liquefied gases used as propellants follow Raoult's Law quite closely over the temperature range involved in filling and in use.

If then a liquefied gas, or a mixture of two or more such gases, is discharged *as liquid* from a container, the pressure in the container (and the composition of the mixture) will remain virtually constant until all the liquid has been discharged.

(a) In *two phase aerosols* the liquefied gas propellant is completely miscible with the rest of the formulation, e.g. a space insecticide consisting of propellant 12/11 mixture and a concentrate based on odourless distillate. The liquid contents are driven out by the pressure in the gas phase. The composition of the propellant/concentrate mixture and the internal pressure of the aerosol remain virtually the same until all the contents have been discharged, ensuring a uniform spray performance throughout the life of the container.

When the valve is opened the liquefied gas, as it leaves the spray head, expands rapidly to produce 200 or 300 times its volume of gas. This effect, coupled with the action of the valve orifices, etc., atomises the product being dispensed. The degree of atomization and hence the coarseness or particle size of the spray is determined both by the composition of the propellant and by its proportion in the formulation, as well as by the structure of the valve used. Temperature is, of course, an important consideration ; a product formulated to give a suitable spray at 50–70°F would not dispense

satisfactorily at temperatures below freezing and similarly it might develop an undesirably high pressure for its container in the tropical sun.

Most space sprays, hairlacquers, colognes and surface coatings are dispensed by the two-phase system, employing from say 85% down to 30–40% by weight liquefied gas propellant in the formulation.

(b) *Three phase aerosols* containing two liquid and one gaseous phase are most commonly water-based products. Water is immiscible with all the fluorinated hydrocarbon and hydrocarbon propellants used in aerosols, but it can be emulsified with them to varying degrees by using emulsifying agents and by shaking the container before use. Shaving creams, foams and shampoos can virtually be regarded as two phase sprays containing just sufficient propellant to expel the contents and expand the emulsion into a foam. Water-based furniture polishes and starch sprays on the other hand contain a small proportion of propellant to expel the contents and rely to a large extent on the assistance of a mechanical break-up valve to produce a coarse spray. Foams and water-based polishes of these types usually contain only 5–15% of liquefied gas propellant.

(c) More recently space sprays such as air fresheners have been formulated with a different water-based system which uses a higher liquefied gas propellant content of the order of 30–40%. Emulsifiers and shaking provide mixing of the aqueous and propellant phases. The dip tube is sometimes restricted to limit the rate of discharge and an orifice in the valve housing inside the vapour phase allows gaseous propellant to join the liquid phase and assist atomization. The valve is of the mechanical break-up type.

(d) Powder aerosols are also three phase systems, with the finely divided solid phase suspended in the liquid propellant phase, e.g. talcs.

Compressed Gas Systems

In this type of aerosol, the propellant is almost entirely present as gas in the head space, usually about one-third of the total volume. As the contents are discharged the pressure falls progressively. Higher pressures are thus required than with liquefied gases–for example a typical pack would be charged initially with nitrogen gas to a pressure of 90–100 p.s.i.g. to ensure that sufficient pressure remained to expel the last of the contents. Viscous products, such as toothpastes and handcreams, are dispensed in this way with nitrogen, where the main object is to expel the contents without appreciable change. The cost of the propellant is negligible.

Where a degree of solubility of the propellant in the formulation can be achieved, compressed gases are used for foam products or, with the aid of mechanical break-up valves, for very coarse sprays. The outstanding use

(largely in the U.S.A.) is of nitrous oxide/carbon dioxide mixtures for dispensing whipped cream toppings. Other food uses have been slow to follow. Nitrous oxide is occasionally used in shaving creams, and carbon dioxide in de-icing and similar coarse sprays ; both have been used in motor starter sprays in the U.S.A. but it is unlikely that the use of compressed gases will increase for applications where any real degree of atomization is required.

Some "mother-and-daughter" packs use nitrogen to boost the pressure of the larger unit and so facilitate transfer of its contents to the handbag container.

A comprehensive account of compressed gas propellants for non-food products is given by Webster[1].

Chlorofluorocarbon Propellants

The use of dichlorodifluoromethane as a hazard-free refrigerant was first developed in the U.S.A. in 1931. Other fluorinated hydrocarbons followed as the refrigeration and air-conditioning industries expanded. These compounds are now made in countries throughout the world to the extent of over 300,000 tons a year and for some years the demand for use in aerosols has exceeded that for refrigeration. They are manufactured in the United Kingdom under the trade names "Arcton" and "Isceon".

The outstanding advantages of this class of liquefied gas propellant are their freedom from hazard and their high degree of stability and chemical inertness. The liquids are colourless, giving colourless vapours with faint and not unpleasant odours. They do not damage furnishings or fabrics. Some of the physical properties of the three propellants in most common use (12, 11 and 114) are given in *Table 1*.

The versatility of these three propellants is almost unlimited. A propellant can be made to measure for almost every non-food application by selecting the right compound or mixture. The most widely used source of pressure is *propellant 12* ; it exerts a pressure of about 70 p.s.i.g. at 21°C (70°F) and is thus only used alone where the overall pressure is reduced by the other components of the formulation, e.g. in aerosol paints. More commonly it is mixed with *propellant 11* to reduce the pressure ; this also increases the solvent power of the propellant without the risk of damage to gaskets, etc. Throughout the world the most widely supplied mixture is propellant 12/11 50/50—equal weights of 12 and 11—with a pressure of about 37 p.s.i.g. at 21°C (70°F). It is the basis of many space insecticides, air fresheners and hair lacquers.

Although the chlorofluorocarbons are extremely stable, the most asymmetric molecule of the three, propellant 11 (CCl_3F) is less resistant to hydrolysis than the others and can also react under certain conditions with the lower alcohols. In addition, it can affect certain classes of perfume

Table 1

Properties of liquefied gas propellants, solvents and pressure depressants used in aerosols

	Formula	Molecular Weight	Boiling Point at 1 atm.		Gauge Pressure at 21°C (70°F) psig or * in Hg vac	Density of liquid at 21°C (70°F) g/cc.	Flammability or Explosive Limits (% in air v/v)	Toxicity U.S. Underwriters Laboratories Classn. Group
			°C.	°F.				
Propellant 12 (dichlorodifluoromethane)	CCl_2F_2	120·9	−29·8	−21·6	70	1·325	Non-flammable	6
Propellant 11 (trichlorofluoromethane)	CCl_3F	137·4	23·8	74·8	2·6*	1·485	Non-flammable	5a
Propellant 114 (1.2 dichlorotetrafluoroethane) ..	$CClF_2.CClF_2$	170·9	3·6	38·4	13	1·47	Non-flammable	6
Vinyl chloride	$CH_2:CHCl$	62·5	−13·9	7·0	35	0·91	4–22	4–5†
Propane	C_3H_8	44·1	−42·1	−43·8	110	0·50	2·15–9·1	5b
*n*Butane	C_4H_{10}	58·1	−0·5	31·1	17	0·58	1·85–8.1	5b
*iso*Butane	C_4H_{10}	58·1	−10·2	13·6	30	0·56	1·8–8·4	5b
Methylene chloride	CH_2Cl_2	84·9	40·2	104·4	8*	1·32	Non-flammable	4–5
1.1.1.-Trichloroethane .. .. .. ("Genklene")	$CCl_3.CH_3$	133·5	74–77	133–139	26*	1·29	Non-flammable	4–5†

Note: †Not classified but estimated to be between Group 4 and 5.

adversely. Thus for water-based products and a number of cosmetics, such as colognes and perfumes, propellant 12 is used alone or in mixtures with *propellant 114* which is characterized by its outstanding stability and is practically odourless. Propellant 12/114 mixtures in proportions such as 10/90, 20/80 and 40/60 are commonly used.

The gauge pressures of a range of 12/11 and 12/114 mixtures are given in *Table 2*.

Table 2

Vapour pressures of propellant mixtures at 21°C (70°F.)

Propellant 12/11 mixtures	Gauge pressure p.s.i.g.	Propellant 12/114 mixtures	Gauge pressure p.s.i.g.
35/65	27	10/90	20
40/60	30	20/80	27
50/50	37	30/70	34
60/40	44	40/60	40
65/35	47	50/50	46

Flammability

The propellants are non-flammable and have flame suppressant properties ; indeed, it is sometimes possible to formulate non-flammable products (judged by, say, the flame-projection test) containing flammable solvents, by incorporating chlorofluorocarbon propellants. The propellants do not form explosive mixtures with air in any proportion.

Toxicity

The (U.S.) Underwriters Laboratories Classifications for the vapours of propellants 12, 11 and 114 are Group 6, 5a and 6 respectively. Group 6 is defined as "Gases or vapours which in concentrations up to at least about 20% by volume for durations of exposure of the order of 2 hours do not appear to produce injury", i.e. virtually free from toxicity under all normal conditions of use. For comparison purposes, carbon dioxide is classified in Group 5a and has an MAC (maximum allowable concentration for continuous working) of 5,000 ppm (0·5%) by volume.

Thermal Stability

Propellants 11, 12 and 114 begin to decompose in contact with open flames or red-hot surfaces to form acidic products and sometimes traces of phosgene, which would be hazardous if inhaled in sufficient quantity. Fortunately, the sharp, acrid odour of the acidic products gives sufficient

warning of their presence. Nevertheless, work areas near filling plant should be adequately ventilated when, for example, welding is in progress and heating installations should avoid red hot surfaces or naked flames.

From the aerosol user point of view, it is considered that the quantities involved make the possibility of hazard from such decomposition extremely slight and this is borne out by the trouble-free record of fluorocarbon propellants and refrigerants in this respect over many years. A number of cases where propellant 12 was cited[2] as a cause of poisoning due to thermal decomposition were discussed by Downing and Madinabeitia[3] in 1960. They pointed out that the possibility of decomposition of the fluorinated compounds could not be ignored, and that there was no intention of minimizing the toxicity of some of the products formed ; but they concluded that there was insufficient evidence to implicate propellant 12.

Quite independently, work has been carried out in our laboratories to simulate the use of three types of domestic convector heater in a small unventilated room containing the vapour of a number of halocarbons. An atmosphere *maintained at a constant composition* was fed to the intake ports of the heaters and the effluent air analysed for breakdown products. The convection rate of each heater was measured. The results obtained with an atmosphere containing 1,000 ppm (0·1%) by volume have been used to estimate the concentrations of toxic breakdown products which could result after 10 minutes in a small sealed room of 1,000 ft.^{3} (28 m^3). These estimates are given in *Table 3*.

Consider first the estimated concentrations from the most toxic decomposition product, phosgene, which has a maximum allowable concentration (MAC) for continuous working of 1 ppm by volume.*

(i) With one exception, phosgene was not detected in the effluent gases from the electric and gas convector heaters, but the paraffin heater favoured its formation. Only with methylene chloride was the M.A.C. reached or exceeded.

(ii) With the paraffin heater, 5·7 oz of propellant 11 in the atmosphere produced about the same concentration of phosgene as 2·6 oz of vinyl chloride. Propellant 12 produced none and propellant 114 a negligible amount.

*The M.A.C. is the maximum average atmospheric concentration of contaminants to which persons may be exposed for an 8-hour working day without injury to health. These values are based on the best available information from industrial experience, from experimental studies and when possible, from a combination of the two. They should be used as guides in the control of health hazards and should not be regarded as fine lines between safe and dangerous concentrations. They represent only conditions under which it is felt that workers may be repeatedly exposed, day after day, without adverse effect on their health. The figures listed refer to weighted average concentrations of an 8-hour working period rather than a maximum which is not to be exceeded even momentarily. M.A.C. figures are published by the American Conference of Governmental Industrial Hygienists and are reviewed annually. They are used by the International Labour Office, and have also been used since 1960 as a basis for the "maximum permissible concentrations" published in the United Kingdom by the Ministry of Labour.[4]

Table 3

Estimated concentrations of decomposition products after 10 minutes in a sealed room 1,000ft.^{3} (28m^3) containing 1,000 p.p.m. (0·1 %) by volume of halocarbon and a domestic convector heater

Halocarbon	Weight required* to give 1,000 p.p.m. v/v — oz	Electric convector heater convection rate 950 ft^3 (27m^3)/hr			Gas convector heater convection rate 1,000 ft^3 (28m^3)/hr			Drip-feed paraffin convector heater convection rate 140 ft^3 (4m^3)/hr		
		Estimated concentration ppm by volume in a room of 1,000 ft^3 (28m^3)								
		Phosgene	HCl	HF	Phosgene	HCl	HF	Phosgene	HCl	HF
Propellants										
Vinyl chloride	2·6	nil	nil	—	nil	33	—	0·12	12	—
Propellant 12	5·0	nil	nil	<0·16	nil	8	5	nil	12	4·7
,, 12/11 50/50†	5·5	nil	nil	0·39	nil	20	4	0·07	40	10·9
,, 114	7·1	nil	nil	<0·16	nil	7	1·7	0·02	9·5	10·7
Solvents and pressure depressants not used alone as propellants										
Methylene chloride	3·5	nil	nil	—	2·1	67	—	2·0	35·6	—
Stabilised 1.1.1.Trichloroethane ("Genklene") ..	5·5	nil	21	—	nil	33	—	0·19	23·8	—
Propellant 11	5·7	nil	nil	0·64	nil	33	3	0·14	71·5	17·8

Notes: *assuming complete vaporization at 20°C.
†estimated from separate propellant 12 and 11 results.

(iii) In all cases where phosgene was produced, appreciably greater concentrations of the acidic gases were formed, confirming that these would have given adequate warning.

All the compounds tested have been used in aerosols and in most cases the quantities involved could conceivably be discharged from standard aerosol containers in the home. Under certain circumstances toxic products are undoubtedly produced with all the compounds, but consideration of (i)–(iii) above, and the fact that deliberately unfavourable conditions were created, suggests that this would not constitute a hazard to health.

Chlorocarbon Propellants

Methylene Chloride (CH_2Cl_2)

Methylene chloride is a non-flammable liquid boiling at 40·2°C. It is one of the least toxic of the chlorinated solvents (MAC=500 ppm v/v, Underwriters Laboratories Group 4–5). Although it has an anaesthetic effect if breathed at high concentrations, the quantities involved in aerosols do not constitute a real user hazard in this respect.

It is used in aerosols in its own right as a solvent, to depress the flammability of other solvents, as a co-solvent to increase the solubility of some ingredients in propellants and as a cheaper substitute for part of the propellant 11 in 12/11 mixtures. As a pressure depressant for propellant 12 its effect is very similar to that of propellant 11.

It has, however, a number of technical disadvantages which limit its use in aerosols. It hydrolyses more readily than propellant 11 which can increase corrosion problems. It has a more defined smell and this, coupled with the higher hydrolysis rate, can seriously affect fragrances and perfumes used in aerosols. It has a marked solvent and swelling effect on elastomers[5], and resistant materials must be used in valves, etc. Its strong solvent action also occasions caution when used in household aerosols; we have found that the misuse of an aerosol containing more than 15% methylene chloride, by applying from a short distance, can damage synthetic fibres such as acetate and triacetate rayons.

Although these disadvantages limit its range of applications and the proportion which may be used, methylene chloride has already established itself as a valuable raw material in the aerosol industry.

1.1.1-Trichloroethane ($CCl_3.CH_3$)

Stabilised grades of this non-flammable solvent are sold under the trade names "Genklene" (ICI) and "Chlorothene" NU (Dow). 1.1.1-trichloroethane has a similar low toxicity to that of methylene chloride (MAC=500 ppm, v/v) but its higher boiling point (ca.76°C) makes it a rather safer solvent for cold cleaning. It is believed, in general, to have less effect on the elastomers

used in valves and little or no effect on textiles, but this apart, it shares the disadvantages of methylene chloride listed above. Its pressure characteristics in mixtures with propellant 12 are very close to those of propellant 11. It is used as a solvent in aerosols (e.g. for cold cleaning, spotting) and to reduce the flammability of other solvents. Appreciably more costly than methylene chloride, it is not likely to be considered solely as a cheaper substitute for propellant 11.

Vinyl Chloride (CH_2:$CHCl$)

Vinyl chloride is a liquefied gas, boiling at −13·9°C. Its vapour pressure is very similar to that of propellant 12/11 mixture. It has an MAC of 500 ppm v/v and, although not classified by the Underwriters Laboratories, its toxicity would appear to place it between Groups 4 and 5. At higher concentrations it has an anaesthetic effect but the quantities which might be used in aerosols are never likely to create a user hazard in this respect. Vinyl chloride is cheaper than the fluorocarbon propellants, is a stronger solvent and has a higher expansion ratio on evaporation. On the debit side, it is highly flammable and forms explosive mixtures with air in the range 4–22% by volume. It has a marked swelling effect on elastomers and possesses a pronounced odour. It is manufactured almost exclusively for polymerization to PVC and for the production of allied co-polymers; published work[6] has recommended that it should contain a stabiliser if used in aerosols.

To the best of my knowledge vinyl chloride has not been used commercially in aerosols in the United Kingdom. In a few European countries, and in Japan, it has been used as a primary propellant and two manufacturers in the U.S.A. offer blends of propellant 12 or 12/11 and VC. One of these firms[6] reports that vapour mixtures of vinyl chloride and propellant 12/11 50/50 are non-flammable if the VC content is below 45% v/v, i.e. 29·4% on a liquid weight basis; because of fractionation the actual amount of VC that can be tolerated is 22% w/w, hence their blend is offered as 78% 12/11 50/50+22% VC.

Hydrocarbon Propellants

Propane (C_3H_8), *n*- and *iso*butane (C_4H_{10}) are liquefied gases. They are virtually non-toxic, being classified by the Underwriters Laboratories in Group 5b. Commercial grades vary in composition according to source, but mixtures of two or more of the hydrocarbons provide pressures suitable for aerosol dispensing. For example, a mixture of 50% *n*butane, 25% *iso*butane and 25% propane gives about the same pressure as propellant 12/11 50/50.

The hydrocarbon propellants are low-priced. They are immiscible with, and have a good stability in, water and, unlike the fluorocarbon propellants,

have densities less than 1. These properties all favour the hydrocarbons for water-based applications such as furniture polishes, where small proportions of propellant are used in three phase systems.

The major disadvantage of the hydrocarbons is their high flammability and the fact that they form explosive mixtures with air at quite low levels (<2% by volume). The U.S. Bureau of Mines[7] found that the flammability of pure *n*butane could be suppressed by mixing it with three times its volume of propellant 12. Work which we carried out with commercial butane has shown that about the same figure applies for propellant 12/11 mixture ; 3:1 by volume is equivalent to about 13% butane by weight in the mixture. A second serious disadvantage is that the hydrocarbons often present odour problems due to impurities which are sometimes difficult to remove from containers, etc., as well as affecting filled aerosols.

I am not aware of any non-aqueous aerosols marketed in the United Kingdom with hydrocarbons as the only propellant. Such aerosols are, however, packed in France and a number of European fillers use a proportion of hydrocarbon with fluorocarbon propellants to reduce cost. In the U.S.A. one manufacturer markets two blends : 12/11/*iso*butane 45/45/10, and 12/114/butane 9·1/82·4/8·5—this last mixture being offered for perfume aerosols. Propane is occasionally used in the U.S.A. mixed with propellant 11 or methylene chloride to depress its pressure and suppress flammability.

As yet, few of the water-based space sprays containing larger amounts of hydrocarbon propellant (Liquefied Gas System (c) above) have appeared on the United Kingdom market and it is too early to say whether their performance will equal that of the established space sprays or how much the extra cost of valve, lacquered container and formulation work will be outweighed by savings in solvent and propellant, also the extent to which special storage and transport conditions will be necessary in the distributive chain.

Flammable Versus Non-flammable Propellants

A paper on the flammability of propellants is being read at this Symposium, so that I have deliberately avoided entering the lists and starting what our American friends call a "Hassle". National Aerosol Associations, Government bodies, fillers and propellant manufacturers throughout the world are debating what should or should not be done to ensure the safe transport of aerosols and the protection of the user. It is foolish to emulate the ostrich, but it is equally important to ensure that the good record of aerosols over many years is not endangered by departing too rapidly or radically from well tried practices.

(*Received : 19th March 1963*)

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Discussion

MR. C. BLOOM: Propellants 142b and 152a have been claimed to be good solvents for certain drugs and they might, therefore, serve a quite useful role in the cosmetic and pharmaceutical fields. Do they have any serious disadvantages and what progress, if any, has been made towards their commercial exploitation?

THE LECTURER: Propellants 152a ($CH_3.CHF_2$) and 142b ($CH_3.CClF_2$) boil at −24°C. and −9.4°C. respectively and have the relatively low densities of 0.91 and 1.12 g/cc at 21°C. I believe that 152a was first manufactured in the U.S.A. for use as a refrigerant in an azeotropic mixture with 12, designated refrigerant 500. To the best of my knowledge propellants 152a and 142b are only offered in commercial quantities by one American supplier who claims that 152a has unique solvent characteristics and recommends 142b for cosmetics such as perfumes, either alone or in mixtures with 114. It is noteworthy that both propellants can form flammable mixtures in air (152a : 5.1–17.1%, 142b : 9.0–14.8% v/v). There has been no demand for these propellants in the United Kingdom and the high cost associated with small scale production would only warrant their adoption where they had outstanding advantages.

MR. A. HERZKA: Is it likely that your company will supply, in the near future, propellant blends similar to the two listed at the end of your paper?

THE LECTURER: No.

MR. A. HERZKA: You refer to odour problems when using hydrocarbon propellants. Is it not possible for such materials to be supplied free from obnoxious odours, as is the case in the U.S.A.?

THE LECTURER: My company does not supply, or use, unstenched hydrocarbons for aerosols, but it is my understanding from fillers that such hydrocarbons supplied on the United Kingdom market still have some residual odour. Perhaps another participant would care to comment further.

MR. D. S. RANDALL: In destenched butane there is a residual odour, but we consider our products to be almost comparable with American and European

hydrocarbons, which we have tested. Work continues on this problem, and we hope to have thoroughly acceptable products in the near future.

MR. H. F. FROST : I assume, from the nature of the results in *Table 3*, that the gas convector heater used in the experiment was not the modern type in which the combustion products go up the flue and hot air only is circulated, but the older free-standing type where all the combustion products were released into the room. Is this so?

THE LECTURER : This is true. The convector heaters used in these experiments were standard domestic appliances which rely on convection of air and which were not fitted with flues or chimneys.

DR. P. H. WITJENS : Are any quantitative data known on the formation of $COCl_2$ from CH_2Cl_2 vapour in the presence of a radiant bathroom heater (e.g. metal coated ceramic heating bar)?

This problem is of significance in Holland as some new buildings have small bathroom cubicles so heated, with poor ventilation, where hair sprays containing methylene chloride may be used.

THE LECTURER : I know of no data referring to these specific conditions. I would think, however, that since the quantity of propellant, or methylene chloride, involved in one application to a woman's hair would be small, the concentration of phosgene produced would be correspondingly minute.

DR. H. KÜBLER : The toxicity values for vinyl chloride and 1,1,1-trichloroethane in *Table 1* do not agree with those I have quoted. I must admit that I did not determine the value for the latter, but I know that the vinyl chloride value is proven.

THE LECTURER : I presume you are referring to the U.S. Underwriters Laboratory's classification groups for vinyl chloride and 1,1,1-trichloroethane. To the best of my knowledge neither compound has been classified by the Underwriters Laboratories and the figures I quoted were estimated from a review of available data.

The data on vinyl chloride is somewhat conflicting, e.g. the findings of Torkelson, which do not agree with those of the Battelle Institute, quoted by you. Toxicity data on the 1,1,1-trichloroethane is limited. However, because of the anaesthetic properties of vinyl chloride and bearing in mind the fact that the current MAC figure for each compound is 500 ppm, as for methylene chloride, it seemed reasonable to me to suggest that both would fall within the same Underwriters Laboratories Group as methylene chloride, i.e. Group 4–5.

DR. H. KÜBLER : You are quoting estimated concentrations of decomposition products of halocarbons, in *Table 3*, whereas the figures quoted by

me are exact. I consider temperature to be decisive for decomposition, which must be observed only above 500°C.

THE LECTURER: I would like to assure Dr. Kübler that the actual measurement of the decomposition products leaving the convector heaters was carried out very precisely and was not "estimated". Phosgene, for example, was measured by individually calibrated Dräger tubes and by absorption in aqueous aniline to form diphenyl urea. I have used the word estimated only in so far as I have interpreted these results in terms of an atmosphere in a sealed room, i.e. attempted to relate the scientific tests to extreme conditions under which an aerosol might be discharged. Temperature is indeed an important factor but other effects such as humidity and metal surfaces are also important so far as decomposition is concerned.

MR. J. C. THORNTON: With regard to the thermal decomposition of halocarbons detailed in *Table 3* of your paper, were the temperatures of the elements in the three different convector heaters measured?

THE LECTURER: No. The experiments were carried out with standard domestic appliances to give realistic conditions rather than to obtain additional academic information.

MR. H. F. FROST: Have you examined the decomposition of propellants drawn through a lighted cigarette in the "domestic" experiments?

THE LECTURER: No. We have, however, carried out work on the problem of smoking cigarettes in atmospheres containing the vapour of chlorinated hydrocarbons and the results were published by Little [*Brit. J. Ind. Med.* **12** 304 (1955)]. In no case was phosgene found in the vicinity of the glowing tip of a cigarette smoked in the contaminated atmospheres, and even when a trace of phosgene was added to the atmosphere, it was destroyed by passage through the cigarette being smoked.

SOCIETY OF COSMETIC CHEMISTS OF GREAT BRITAIN

Symposium on Aerosols

A SYMPOSIUM on Aerosols organized by the Society, took place at Southport on 24th and 25th April 1963. It was attended by over 150 participants from France, Western Germany, Sweden, the Netherlands, Australia and the United Kingdom.

Delegates were welcomed by His Worship the Mayor of Southport, Alderman Dr. S. J. Hepworth, J.P. The President of the Society, Mr. G. A. C. Pitt, afterwards thanked the Mayor for his kind remarks and then formally opened the Symposium. The Symposium was followed on the afternoon of the 25th April by a lively Brains Trust. A variety of questions was put to the panel consisting of Messrs. M. N. Conville, P. Dyson, J. A. T. Fisher, R. A. Gunn-Smith, and J. Pickthall. Mr. A. Herzka was the Question Master.

A Civic Reception was given by the Mayor and Corporation of Southport on the evening of the 24th April at the Palace Hotel.

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.
Friday, 6th December 1963.
Thursday, 23rd January 1964.
Thursday, 27th February 1964.
Monday, 23rd March 1964.
Thursday, 7th May 1964.

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.

Annual Dinner and Dance

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

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, and the following Programme has been arranged. Participation is permitted only when application has been made on the appropriate form, and the fee duly paid.

The Symposium registration fee is £3 3s. for each participant who is a member of one of the Societies of Cosmetic Chemists affiliated to the International Federation of Societies of Cosmetic Chemists. 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, Esq., F.R.I.C.

09.25 "The duty to take 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. GOMAHR, 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.

GENERAL NOTICES

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

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

Advertisements: All enquiries regarding advertisements in the British Edition of the Journal should be addressed to Mr. R. D. Miller, Pergamon Press, Ltd., Headington Hill Hall, Oxford.

Subscription: All members of the Society of Cosmetic Chemists of Great Britain receive one copy of each edition free. Further copies at non-member rates. Non-members: £8.8s. per annum, post free, or £1 per issue, post free.

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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 approx. ***£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. All rates are subject to confirmation, because the 1964 trans-atlantic fare structure will not definitely be known until the autumn of this year.

No deposits are required for the time being.

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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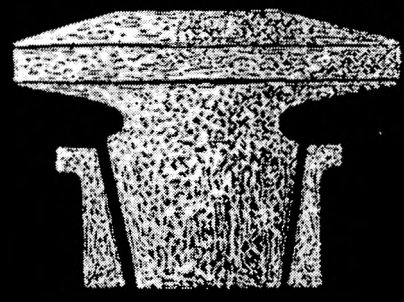

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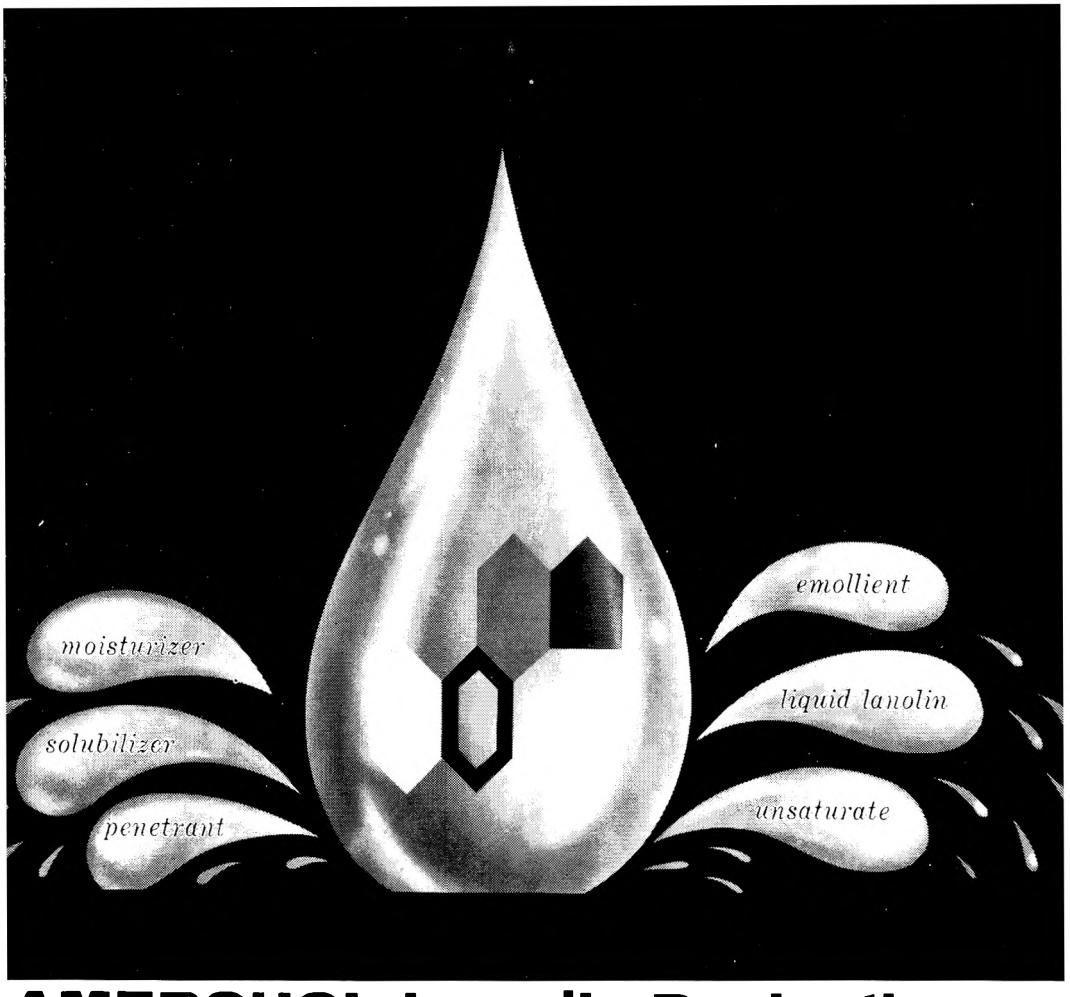

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