The household aerosol: present and future of the world's largest market for spray technology

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The current technology and market for pressurised household aerosol cans is described, with reference to the different products that are sprayed and the requirements for each type of product. The probable future legislative restrictions on volatile organic compounds in many countries are outlined with reference to the repercussions in the current aerosol products industry. It is described how these restrictions will generate new research interest in the more efficient production of sprays, and particularly in the reduction or replacement of hydrocarbon flashing propellants. The problems associated with these aims and their possible solutions are then described.

1. Introduction

The pressurised household aerosol can is found universally in the developed world and in most homes in the developing world. We here use the expression "household aerosol" to describe

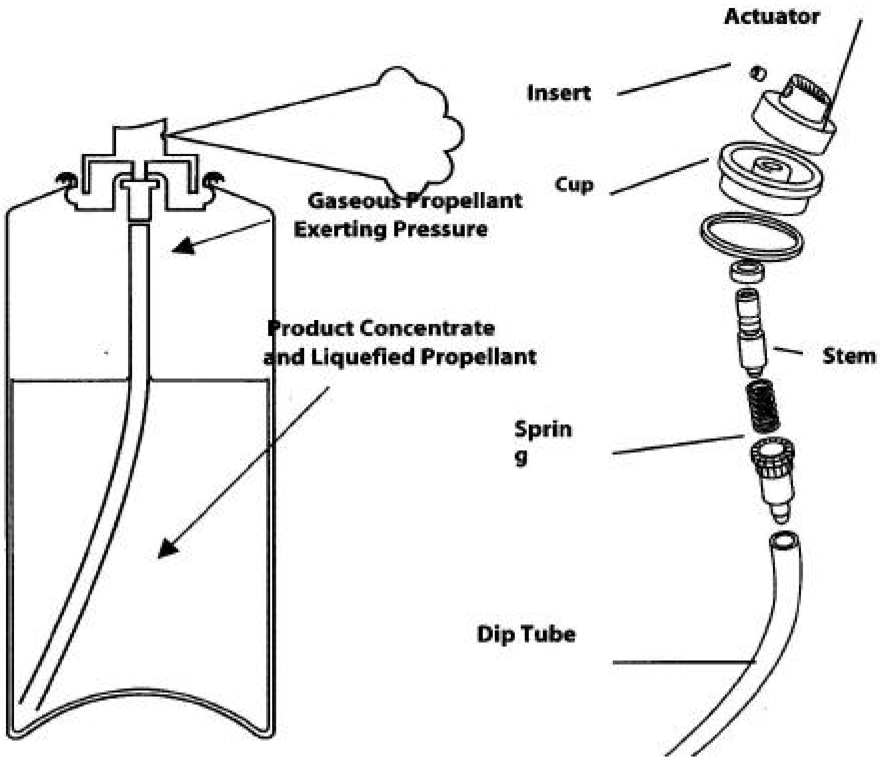

Fig. 1 Generic aerosol can, courtesy British Aerosol Manufacturers Society

Fig. 2 Typical household sprays, from left to right: starch, air freshener with vertical spray, cleaning fluid using trigger pump, and body spray using finger pump.

pressurised cans used for household purposes such as cleaning, polishing etc., and we include the so called "personal care" area, i.e. deodorants, hair sprays etc. Furthermore the use of these devices extends into other areas, such as for lubrication, paint application and de-icing of vehicles. Pressurised aerosol cans are relatively recent in their mass use, with the first examples being insecticide sprays introduced during WW2. Figure 1 shows a typical aerosol can which is pressurised, typically to 4 to 5 bar, using a liquefied gas. That is, the propellant is a low boiling point fluid (b.p. typically between 220K and 270K). Up to 15 years ago this fluid was a refrigerant such as Dichlorodifluoromethane (Refrigerant 12), which is of course a CFC and is now banned because it is a so-called greenhouse gas. The reasons for use of liquefied gas propellant and the replacements of the first CFC propellants are described in the next section which provides an overview of the current technology.

2. The present technology and markets

2.1 Present technology

Figure 2 illustrates some typical household spray products. The starch and air freshener cans on the left both utilise flashing propellants. The air freshener has a vertical nozzle, in line with the can axis, for ease of use. It also uses a more modern injection moulded actuator that forms part of the cap of the aerosol can. The two *pump sprays* on the right in Fig. 2 are shown to illustrate this technology, which tends to complement rather than compete with the pressurised aerosol can format. This pump technology is sometimes used either when droplet size is not of great importance (for example for the window cleaning spray, second from the right in Fig. 2) or when a fine spray can be produced because the liquid has a low viscosity and surface tension and a low flow rate is needed (for example for the body spray on the right in Fig. 2). In these examples the *trigger pump* pumps the liquid to pressures up to around 5 bar. The *finger pump* achieves rather lower pressures. These devices have a restriction that the liquid to be sprayed must not be sensitive to contamination due to its prolonged contact with the air in the bottle. Although the pumps are relatively expensive to manufacture, they do not require the expensive high pressure filling equipment needed for pressurised aerosol cans, and also refilling is straightforward. All the devices in Fig. 2 use a miniature swirl atomizer insert.

For pressurised aerosol cans, the principal replacement for CFC propellants has been liquefied hydrocarbon (HC), principally butane but with "blends" with, mainly, propane to "fine tune" the boiling point. These hydrocarbons are not powerful greenhouse gases and their thermodynamic properties are sufficiently close to CFC's for the changeover to be relatively straightforward for the industry with little noticeable deterioration in spray quality for different applications. There is an appreciation of the potential danger of hydrocarbons due to flammability and, in certain industrial applications in Europe, a Voluntary Code of Practice permits the use of non – flammable Hydrofluorocarbon (HFC) propellant instead of HC's. For all propellants, and as seen in Fig. 1, a simple spring loaded valve is attached to the can and, on depression by the injection moulded polymer attachment on top of the valve (referred to as an *actuator*) the can pressure forces the liquid phase propellant-product solution, or mixture, up through the *dip tube* and around the valve stem, into a central vertical channel in the actuator. For most cans the channel inside the actuator turns through approximately 90 degrees in order to produce a horizontal spray. Generally it is not possible to injection mould both the actuator and the final nozzle and orifice as one unit, however see the descriptions of novel technologies later in this paper. Thus the final nozzle is a separate injection moulded item which is referred to as an *insert*. As shown schematically in Fig. 3, with very few exceptions these inserts are either of the *simple orifice* type, or they incorporate a pressure swirl atomizer which are referred to as a *Mechanical Break Up Unit* or "*MBU*".

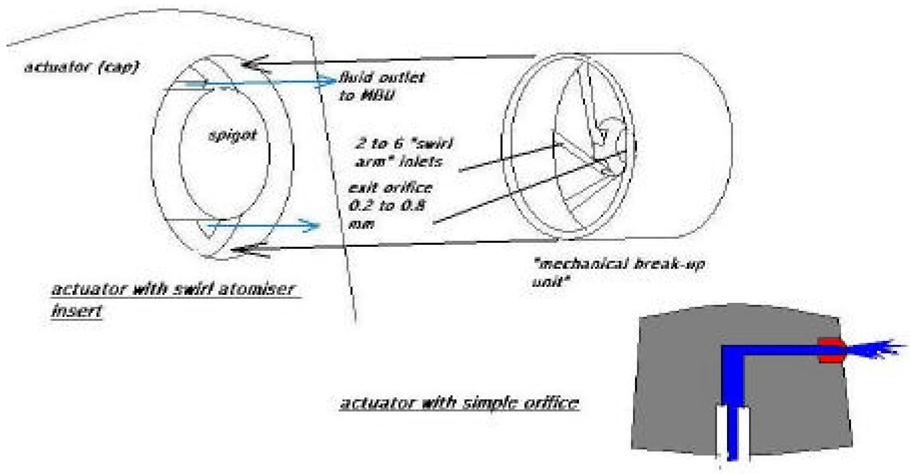

Fig. 3 MBU and simple orifice designs

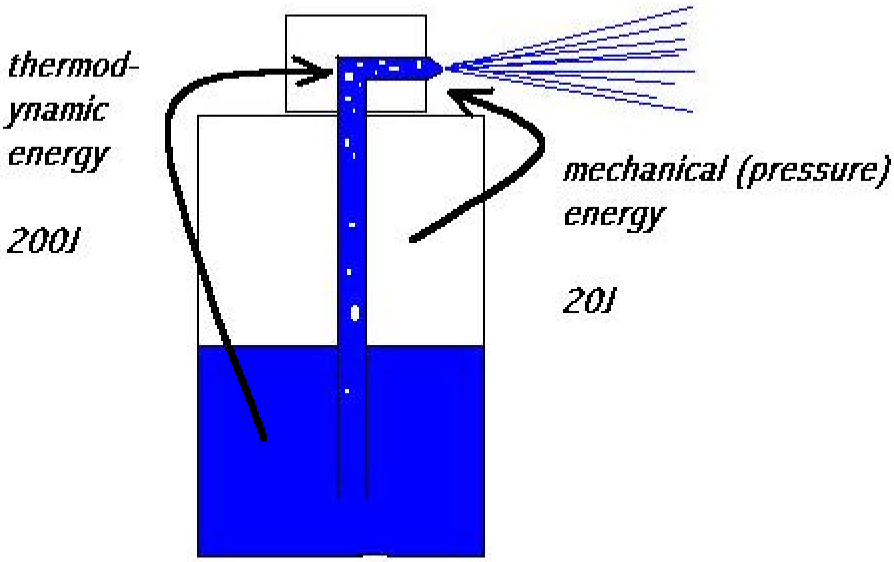

Fig. 4 Energy sources for flashing propellant

It is useful at this point to recognise the great advantages of using a flashing (liquefied) propellant. An aerosol can is typically safety accredited to around 12 bar internal pressure and, allowing for use at high ambient temperature and for storage in the hold of an aircraft at low ambient pressure, safety margins limit the internal can pressure to typically 4.5 to 5 bar at STP for the surrounding environment. For "inert" compressed gas propellants such as Nitrogen, a can pressure around 8 bar is possible. All of the energy for atomization must be contained in a small (typically less than 0.5 litre) can and it is desirable that at least half the can contents, when new, should be liquid. As illustrated in Fig. 4 we can consider the mechanical energy available for atomizing where this is simply the work done by the gas pressure pushing the liquid out of the can: this may be typically 20J for a flashing propellant, for which the can pressure does not decrease greatly during evacuation of the liquid due to continual release of new vapour. However if, say, Nitrogen were used to pressurise the can, the can pressure would halve during use giving only 15J approximately of mechanical pumping energy. The flashing propellant is also a source of energy from thermodynamic effects due to its phase change during flow through the device and particularly at the exit. This phase change results in high gas phase exit velocity so that the exit nozzle is effectively a two-fluid atomizer where the gas/liquid mass ratio may be at least 5:1. As shown in Fig. 4 this thermodynamic energy is at least two orders of magnitude greater than the mechanical pumping energy. Thus the following statement can be made:

"Aerosol cans with flashing propellants have enough available energy to achieve any mean drop size that is realistically required and for most types of liquid formulation, even for difficult high viscosity liquids or suspensions: Take away the energy available due to flashing and there are very few applications, which have combinations of large drop size and "easy" liquid properties, such that current technology can be applied to give satisfactory sprays".

Figure 4 indicates bubbles in the dip tube and the actuator. This is inevitable because the pressure drops with the flow along the tube, through the valve and around the bend in the actuator: every drop in pressure changes more of the propellant into the gas phase. An inevitable result of this pressure drop and phase change is that heat is removed to provide the latent heat and this heat comes from the liquid and also the actuator. Thus aerosol cans and their sprays are always cool to the touch when spraying. This cooling action may be important when the sprayed formulation contains oils, such as silicone oil found in antiperspirants: these oils will increase in viscosity and may thus result in larger droplets. Many aerosol cans use a *vapour phase tap* (VPT) to deliberately introduce vapour into the flow in the actuator. The VPT is simply one or two holes in the fitting between the dip tube and the valve, which allows vapour from the top of the can to enter the liquid flowing into the valve. The mass flow of this vapour is relatively very small compared with the flow of liquid phase up the dip tube. This is because the pressure drop across the VPT orifices, which controls the vapour flow, relies on there being a pressure drop in the dip tube from its inlet up to the VPT position: this drop in pressure is very much less than the can pressure. The VPT reduces drop sizes and also, due to the gas blockage effect, reduces the spray flow rate.

2.2 The markets

The size of the pressurised aerosol can market needs to be appreciated in order to understand the economic importance of the industry to many countries. In 2002 the world-wide production exceeded *11 billion units* and the approximate breakdown of this production by regions is shown in Fig. 5. Most but not all of these units are spraying devices, other devices being used in non-spraying formats to dispense mainly gels or foams.

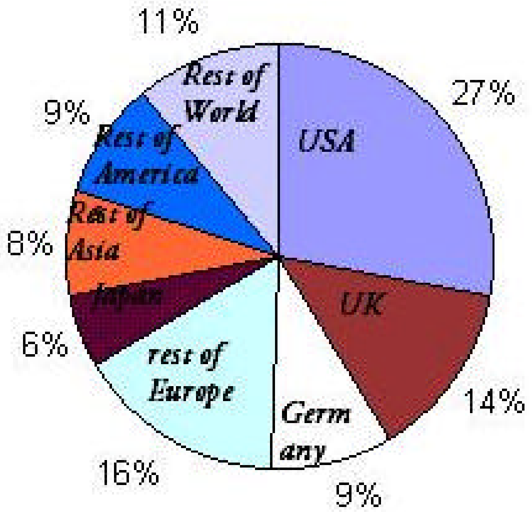

Fig. 5 Division of total world production of 11billion units in 2002.

Of course each unit is of relatively low value, however even allowing for this the value of the total market is comparable with, if not higher than other spray technology areas, including gas turbines, spray drying equipment, agricultural spraying and medical spraying devices. However the published research relevant to the pressurised aerosol industry is completely negligible compared with these other fields. This is due entirely to the use of flashing propellant which makes “good sprays” so easy to produce: a luxury which, as described below, is now coming to an end.

Figures 6 and 7 provide data on production in Europe for 2002 for the main types of application, divided into “personal products”, in Fig. 6, and “household products” in Fig. 7,

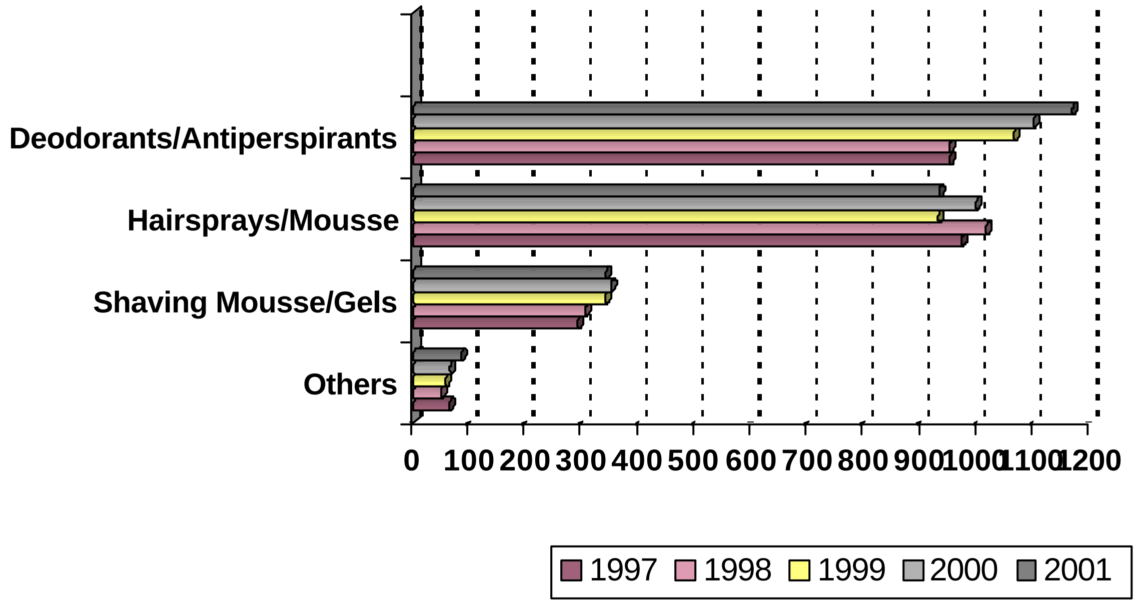

Fig. 6 Personal aerosol production in Europe, thousands of units (European Aerosol Federation)

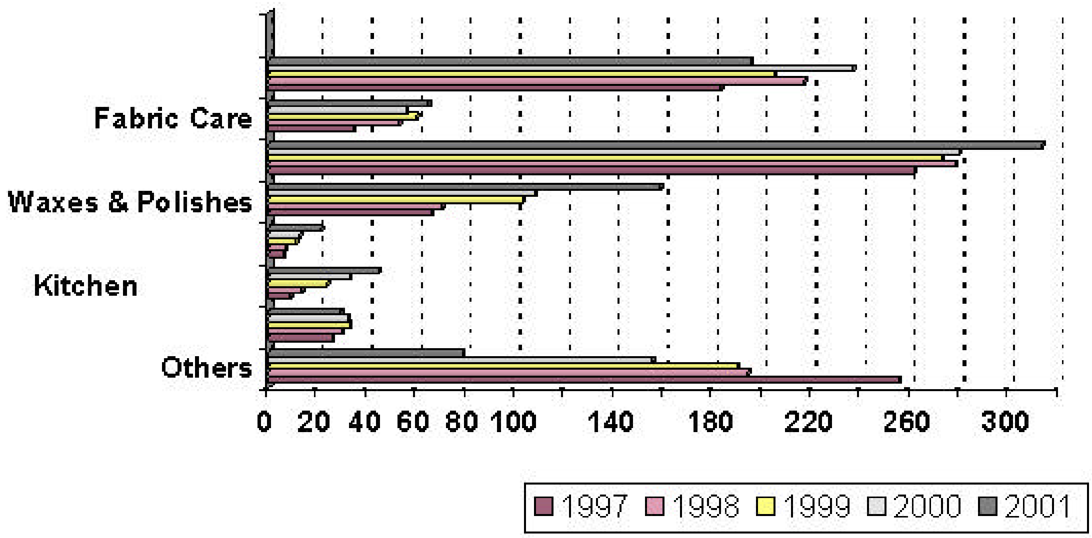

Fig. 7 Household aerosol production in Europe, thousands of units (European Aerosol Federation)

Product Category	CARB VOC limit	Current Products (Europe)	Typical Current Spray Characteristics	Problems
Hair spray	55%	European formulations 80% - 90% VOC (+), butane/propane, polymer in ethanol. European moves to restrict VOCs. Also DME or DME/butane at 30% propellant; 50% alcohol and 15% water. MBU (Swirl) inserts common	Vol Med Dia. 50-80 microns spray angle 30 degrees (+), hollow cone. Flow rate 0.3 to 1.2g/sec. Would like to limit fraction of droplets less than 10micron e.g. less than 5-7%	Require good atomisation, negatively affected by viscosity increase with water addition. Fast drying rate negatively affected by water and increased droplet size. Products must wet out hair effectively. Non - Newtonian with complex polymers in product, extensional viscosity?
Air fresheners	Progressively, 30% to 18% (liquid/ pump sprays)	Typically around 30% butane 68% water, plus fragrance, and emulsifier. Simple orifices common.	Vol Med Dia 30 to 45 microns. Flow rate 0.8g/s. 30degree full cone. 1.5m minimum throw (penetration)	Finer sprays preferred, but must have adequate penetration (throw), difficult to get finer than 30-40 micron with aqueous formulation. Larger particle sizes rapidly settle, taking fragrance with them. Inhalation problems?
Anti-perspirants Personal Deodorants	HVOC 40% and MVOC 10% HVOC 0% and MVOC 10%	Simple orifice with "bull-nose" & VPT. Typ.composition: silicones 13%, hydrocarbon propellant 75%, Aluminium chlorohydrate powder 10%. Powder-free often essentially 97% VOC: 50% ethanol plus propellant plus perfume etc. MBU (Swirl) insert common.	Vol Med Dia 10-20microns. Flowrate 0.75-1g/s. Spray angle 20-30degrees full cone. Vol Med Dia up to 40 microns. Flowrate 0.6g/s. Spray angle up to 40 degrees, full or hollow cone.	Interest in reducing inhalable fraction (sub-7 microns say) currently 20%+. Particulates + silicone = high viscosity: Non flashing spray would be coarse. Cool feel attractive to customer. Replacing ethanol with water can give poor "feel" to spray.
Spray Paints	88% but reducing	Hydrocarbon and/or DME propellant. Typically acrylic resins plus solvent . Solids 10-15%, HC 25-30% solvent 55%. MBU (Swirl) insert, or fan jets.	Ideally Vol Med Dia 40-50 micron. Flowrate 1g/s (+) Spray angle wide rages used.	Water based products for low VOC have drop size challenges. Narrow size distribution ideal: less than 30 microns = drift, greater than 60 microns = runs.
Insecticide	crawling bug 15% (31/1/2/04) flying bug 25% (31/12/04	Hydrocarbon propelled, aqueous or solvent formulation. MBU or simple orifice, with VPT.	For flying insects Vol Med Dia 30-40 microns. Flowrate 0.5-1.0g/s (+). For crawling insects larger droplets and narrow coverage, 1-2.5 g/s	Good penetration with no "fall out" of large drops plus low inhalable fraction: low VOC aqueous formulations have difficulty in achieving this.
Furniture Polish	25% (01/01/94) 17% 31/12/04	Butane propellant, water, butane and solvent, usually MBU insert. Compressed air-driven systems: wax, solvent, surfactant, water: MBU	Vol Med Dia 110 (HC propellant) to 150 microns (+) compressed gas. Flowrate 1.5 g/s (+) Spray angle 30 to 90 degrees hollow cone.	Wax-water solution is viscous and non-Newtonian, problems with reduced solvent and no flashing.

Table 1 Summary of current aerosol products

using the terminology of the industry. It can be seen that there are no signs of reductions in production in Europe, however legislation that may affect production is not yet implemented. The largest volumes of production are for deodorants/antiperspirants, hairsprays, air fresheners and insecticides. Also "other products", not shown here include cans for paints, lubricants and other industrial uses.

3. The challenges

The HFC propellants, e.g. HFC 134a, used for some products, particularly in the USA, remain relatively potent greenhouse gases and they are now subject to increasing legislation in countries abiding to the "Kyoto protocol". The EU has agreed an overall target to reduce emissions of a "basket" of greenhouse gases by 8% by 2010. Domestically DME is another propellant that is used where flammability is a particular issue, however it is a Volatile Organic Compound (VOC) as are, of course, hydrocarbon propellants (HC). VOC's are being subjected to increasing legislative control, with EU controls in force on major sources (IPC, IPPC and Solvents Directive) including Traffic (Auto Oil Programme). In Europe VOC emissions from aerosols are only around 3% of the problem: however they are very "visible" and are considered wasteful or particularly unnecessary because they are not resulting from some reaction in an essential transport or production process. What is classified as a VOC tends to vary from region to region, however in Europe ethanol (alcohol) *is* considered to be a VOC. This means that a deodorant using HC propellant to spray ethanol, with perfume traces, is 100% VOC. In the USA there are severe restrictions on the % of VOC in consumer products, including aerosol can products. The California Air Resources Board (CARB) has led the way with legislation, however it appears likely that the rest of the USA and also Europe will closely follow. However the main "solution" to VOC reduction in the USA has been the use of HFC propellant, and this is not an option for countries, including the EU, which abide with the Kyoto protocol. The problem approaching for the pressurised aerosol industry in these latter countries can be expressed quite starkly:

"*It is very likely that in the near future there will be restrictions in both VOC and greenhouse gas content in cans and there is <u>no permitted flashing propellant available</u> to replace the removed HC or HFC. Thus it will be necessary to make cans spray more efficiently, using lower HC content, or using inert gas propellant or other technologies, whilst at the same time replacing any ethanol in the can, by aqueous liquids*"

Table 1 provides a summary of the present main formats of pressurised aerosols, with the main emphasis on the EU marketplace. Some guidance on CARB legislation is also provided together with a description of some of the problems involved in meeting this type of legislation.

4. Possible solutions

4.1 Overview

It is envisaged that legislation will, in the foreseeable future, be mainly directed at severe reductions in the VOC content of aerosols. Eventually it is quite possible that the complete banning of VOC content may be applied, at least to a certain range of uses. The reduction of VOC leads to two major problems, plus a range of ancillary difficulties related to these problems. These major problems are:

(1) Reduction of VOC inevitably means using less flashing propellant: this leads to less thermodynamic energy for atomising and probably a lower can pressure, so less mechanical energy. An ancillary problem is that for most sprayed formulations, there is significant non-vaporised liquid propellant in the emerging spray so that these "carrier droplets" contain significant (usually HC) propellant. In practice it is likely that removed liquid phase propellant from the can must be replaced, and the only acceptable replacement is water. With its high surface tension, and high viscosity, compared with liquid HC, this gives greater demands on

achieving good atomisation efficiency. There is also a marketing reason for such replacement: the customer may resist purchasing products that do not appear to have much liquid in the can.

(2) The can contents of ethanol and certain solvents will need removal or reduction. Ethanol is the main carrier fluid for many important applications. The problems caused by replacing it with water, which appears to be inevitable as there are no other replacements that are not targeted by legislation, have been described already.

In the next subsections some of the approaches to solving these problems are briefly described.

4.2 Reduced VOC cans with improved actuator fluid mechanics

With the exceptions of work by the groups of the present author, see Sharief et al (*ibid*), and also Sher (*ibid*), there is very little published research that is aimed at improving the designs of actuators and inserts when using flashing propellants. Clearly the large number of patents in the field of actuator and insert design indicates that manufacturers have had an interest in this subject: however examination of current products shows no significant fluid mechanical differences from those of 25 years ago. Sher's work has shown that a chamber prior to the exit orifice causes extra vaporisation to give essentially a two-fluid atomizer with higher gas/liquid gas ratio and thus smaller droplets. That such improvements have not been generally implemented is due to the lack of incentives for the industry, either economic or legislative. Also, incorporating more complex flow control devices inside actuators would add to the number of component parts and thus the cost. However new methods of injection moulding of actuators and inserts as single units now permit more complex internal flow systems to be incorporated. In the present author's group quite intensive work is in progress to derive suitable devices, for different sprayed formulations, that permit acceptable sprays to be achieved with reduced VOC filling of the can.

4.3 Compressed gas aerosols

The use of an inert compressed gas in the can (usually Nitrogen, but Carbon Dioxide has some advantages due to its solubility in water) was the subject of considerable interest in the early 90's. This was driven by worries about the flammability of HC propellants as VOC legislation was then not decided. In particular ethanol based deodorants with compressed gas around 6 bar were marketed with very small MBU's some with exit orifices of 0.15mm diameter. These products failed, possibly due to consumer non-acceptance of the spray quality. One difficulty with compressed gas propellants is that the can pressure drops during use, to perhaps 3 bar. Manufacturers incorporated miniature pressure regulators to maintain constant flow rate during can life, however these could only operate by maintaining the supply pressure to the MBU at the pressure of the can when it is empty, thus wasting pressure energy. In recent years some compressed gas aerosol cans have been introduced successfully to the market., polish sprays in particular. However the relatively large volume median diameter achieved, around 150 microns, does not appear create major difficulties in this application. Special devices have been introduced or patented, but without major market shares, which maintain a high can pressure during can lifetime. One device is a small high pressure storage reservoir inside the can, similar to a soda siphon refill, that gradually bleeds gas into the can. If (inert) compressed gas is to replace flashing propellants for a wide range of applications, then dramatic improvements are required in the efficiencies of the atomizer inserts that are used. There have been proposals for bleeding off some of the gas used to pressurise the can and adding it to the liquid flowing through the actuator. This would create two-fluid atomisation. However this is technically very challenging and simple calculations show that, assuming the new can is 50:50 liquid and gas with 8 bar gas pressure, the available gas/liquid mass ratio for atomization is no more than 0.5% .

4.4 Pumps

Pump technology for household sprays is well established but it has not necessarily been the subject of intensive research and development, reduction of manufacturing costs being an overriding factor. Improved, more easily used pumps, that provide higher pressures than at present are required and these need combining with improved atomizer inserts. Once again some interest has focused on combined liquid-air pumps, which could be used with two-fluid atomizer inserts. In practice there would be a resistance to changeover from pressurised aerosols to pump technology by customers, unless methods can be found for making the pump devices as easy and convenient to use as the pressurised cans.

4.5 "Exotic" devices

More than one person in the field has proposed that electrical power may be utilised with aerosol cans in some way in order to produce or enhance atomization. This power may be from a battery or supplied by applying pressure to piezoelectric transducers. This may be thought to be out of the question due to cost considerations, however it must be recalled that production is in billions so that the volume production savings are immense. Metered dose inhalers for asthma treatment are suffering similar needs for new formats without flashing propellant, although to a lesser extent than for pressurised aerosol cans. Successful portable inhaler products are now widely used, which are battery powered and use ultrasonic atomisation. However the values of these devices are two orders of magnitude greater than those of aerosol cans so that there would be considerable development work needed in order to introduce them to the supermarket shelves.

5. Concluding remarks

This paper has not been a review with descriptions of publications in the field: there are too few relevant publications and open literature to make this worthwhile. Rather the objective has been to draw to the attention of the general "Spray Science Community" to the industry of pressurised aerosols and, in particular, to highlight the major and growing technological problems that this industry will have to meet in the coming years. This is done with the intention that at least some of this community will consider it to be worthwhile to direct their research interests and expertise towards the interesting problems in this field.

Acknowledgements

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