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Project Summary

Aerosol Industry Success in Reducing CFC Propellant Usage

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Part I of this report discusses the U. S. aerosol industry's experience in converting from chlorofluorocarbon(CFC) propellants to alternative aerosol formulations. Detailed examples of non-CFC formulations are provided for 28 categories of aerosol products. Hydrocarbon propellants, which cost less than CFCs, are most often selected as the propellants of choice unless special properties such as increased solvency or reduced flammability are needed. Dimethyl ether is the next most preferred CFC alternative, although it is flammable and a strong solvent. Carbon dioxide, nitrous oxide, and nitrogen are inexpensive and widely available, but have been underused as aerosol prepellants. Special equipment is often needed to add them to the aerosol containers. A variety of alternative aerosol packaging forms are discussed in Part II, with special focus on those most like regular aerosols in characteristics. Advantages and drawbacks of several types of alternative dispensing devices are discussed in detail and examples are provided of the types of consumer products which have successfully utilized these alternatives.

This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Since the early 1970s, scientists have recognized the need to reformulate aerosol products into compositions that no longer contain chlorofluorocarbons (CFCs). Once in the stratosphere, CFCs are bombarded with high-energy radiation from the sun, which splits off chlorine atoms that then react with ozone molecules, reducing them to ordinary oxygen. Although ozone is reformed by natural processes, the overall effect has been one of ozone depletion.

In 1987, a treaty known as the Montreal Protocol was developed and ultimately ratified by 36 nations plus the European Community (EC) calling for the orderly reduction of CFC production according to the following schedule:

- ByJuly 1, 1989: reduction to the 1986 average consumption level, based on ozone depletion potential (ODP);
- By July 1, 1993: reduction to 80% of the 1986 average level, ODP basis; and
- By July 1, 1998: reduction to 50% of the 1986 average level, ODP basis.

However, results of stratospheric studies conducted since the Montreal Protocol show that the original reduction plan is not sufficient to prevent further ozone depletion. Also, some of the chemicals currently available to replace

CFCs, such as HCFC-22 and 1,1,1-trichloroethane, can also deplete stratospheric ozone, although their ODPs are less than those of the CFCs.

Future potential alternatives to CFCs such as HCFC-123, HFC-l34a, and HCFC-141b are currently undergoing extensive toxicological testing that will probably continue until 1992. Some of these compounds are nonflammable, but others are flammable and may not be appropriate for use in certain aerosol products. In the U.S., hydrocarbon propellants may be used unless special properties such as reduced flammability and better solvent action are required.

Dimethyl ether (DME), one preferred CFC alternative, is flammable, a strong solvent, and highly water soluble; it can be used to incorporate water into solution in aerosol products such as hair sprays and personal deodorants. Table 1 compares the physical properties of non-CFC aerosol propellants.

Carbon dioxide, nitrous oxide, and nitrogen are inexpensive and widely available throughout the world, but they have not been used much as aerosol propellants since special equipment is often required to add them to the aerosol containers. Table 2 shows the potential uses of these propellants for several representative products.

HCFC-22 is widely used throughout much of the world as a specialty refrigerant and freezant. Despite its nonflammability and relatively low price (5 times more costly than hydrocarbons, in the U.S.), it is not much used. It is limited by its high pressure, which, makes it necessary to use 40% or less in formulas and to include suppressive solvents or other propellants to keep the aerosol pressure from being excessive. An interesting blend of HCFC-22/HCFC-l42b (40:60) is nonflammable and has a pressure of 63 psig at 70°F (4.43 bar at 21°C). It has been commercialized for perfumes and colognes. HCFC-22 is a good solvent. At up to about 28% propellant, its ethanol solutions are lower in pressure than those of CFC-12 and ethanol.

HCFC-142b is used in a few applications in the U.S. and is presently unavailable elsewhere. It is now made by only one supplier,although a second supply source is being developed. As the methyl homolog of HCFC-22, it has many properties in common with the parent compound, except the high pressure. It is more than 12 times as costly as hydrocarbon propellants in the U.S., which has restricted its aerosol applications.

HFC-152a is close to an ideal propellant, except that it is flammable. It is less flammable than hydrocarbon gases, however, and it has been used with (typically) 70% A-46 (20% mol propane and 80% mol isobutane) to produce a propellant for shave creams, depilatories, and mousse products whose foam surface will not momentarily flash if a lighted match is touched to it. Its composition is: 60.9% isobutane, 9.1% propane, and 30.0% HFC-152a. Since the pressure of the aerosol is about 154 psig at 1300°F (11.0 bar at 55°C), according to the partial pressure of remaining air, an extra-strength can is needed.

HFC-152a is noted for its exceptionally low odor and good solvency. It is used to make less flammable colognes and perfumes, especially for those essential oils that might eventually precipitate high-molecular weight resins, fonds, or substantives in the usual ethanol/hydrocarbon (or pure hydrocarbon) systems. Finally, it can be used with many surfactant systems, to partly destabilize aerosol foams, permitting them to be more readily rubbed out on surfaces and not resist liquefaction. A typical product that uses this property is baby oil mousse, which contains 20 to 30% mineral oil.

In the U.S., since HFC-152a is approximately 8 times the cost of hydrocarbon propellants, the amounts used in formulas are generally in the 2 to 10% range. It is available in the U.S. and Western Europe, and suppliers claim that distribution systems will be set up to greatly increase world access to this propellant and to HCFC-142b.

The future "CFC alternative" propellants identified in Table 1 are presently undergoing acute, sub-chronic, and chronic (lifetime) toxicological testing. To date, the results have shown some variation in relative toxicity,but indications are that all five compounds will probably be approved for commercial use. The official toxicological reports will be issued in 1992 and 1993, but plans are now in motion to build production facilities well before that time.

In the U.S., DuPont has announced that an existing commercial plant is being converted to produce HCFC-141b and HCFC-142b in 1989. A new plant has been approved to produce large quantities of HFC-134a by 1990. Small lot quantities of HCFC-123 are already available as a co-product from an existing DuPont facility. And during 1988, DuPont was issued a U.S. Patent on new technology aimed at co-producing HCFC-123 and HCFC-124 in a single process.

No schedules for HCFC-l24 produc have been published, althougl commercial-scale HCFC-123 plan being built in Maitland, Ontario.

Other CFC suppliers in the U Western Europe, Japan, and other p of the world are also studying t options for phasing out CFCs commercializing various alternatives. major alternative will probably be H 134a, since it will be used to repl CFC-12 in refrigeration, freezant, and conditioning systems.

An imposing number of packag alternatives to the standard aero dispenser are available. Several aerosol containers, but segregate propellant gas, and employ a fing pump, trigger-pump, hand-opera piston action, a metal spring, sc device, or other mechanism to dispe the product or form the propellant within the container as required. Oth take the form of rather specialized, r aerosol containers designed to enable user to create air pressure or prod pressure, or to operate screw-on, fing pump or trigger-pump metering valv The pump-sprays, in all their dive forms, represent the most widely u alternative. Such packaging options stick applicators and pads offer al natives to the aerosol system but do provide sprays; these are only bri described in this report.

Many countries are now supporting accelerated CFC phase-down progra which goes beyond the 1987 Montr Protocol and which is based on the ra commercialization and application of HCFC and HFC alternatives. Table 3 l the aerosol products currently exemp or excluded from the general regulat bans in the U.S. on CFCs for aero uses. They serve life-saving or ot medical purposes or are conside "essential" for other reasons.

Formulation Guidelines

A large number of characteristics m be evaluated when considering p pellants or propellant/solvent co binations that may be used reformulating CFC aerosols. Fla mability, toxicology, solvency, cc availability, solvate formation, solvoly stability, dispersancy, pressure, a compatibility are some of the essen characteristics.

Apart from the CFCs, nonflamma propellants consist of nitrogen, nitro oxide, carbon dioxide, HCFC-22, and few blends of other propellants w HCFC-22. Nonflammable propellants t will be available in the future inclu

Table 1. Physical Properties of Non-CFC Aerosol Propellants

Product	Formula	Boiling Point (°C)	Vapor Pressure (bar) 21°C	55°C	Density (g/mL) 21°C	Flammable Range V.%
n-Butane	n-C_4H_10	-2	1.20	4.79	0.580	1.8-8.6
i- Butane	i-C_4H_10	-11	2.17	7.02	0.559	1.8-8.5
Propane	C_3H_8	-42	7.60	18.17	0.503	2.2-9.5
Dimethyl Ether	$(CH_3)_2O$	-25	4.43	12.40	0.661	3.3-18.0
HCFC-22	$CHClF_2$	-41	8.52	20.92	1.208	0
HCFC-142b	CH_3-$CClF_2$	-10	2.04	6.87	1.123	6.7-14.9
HFC-152a	CH_3-CHF_2	-25	4.42	12.36	0.911	3.9-16.9
Carbon Dioxide	CO_2	-78	58.45	N/A	0.721	0
Nitrous Oxide	N_2O	-88	52.47	N/A	0.718	0
Nitrogen	N_2	-155	N/A	N/A	N/A	0
		Future	Propellants			
HCFC-123	$CHCl_2$-CF_3	28	-0.2	1.7	1.470	0
HCFC-124	$CHClF$-CF_3	-11	3.22	8.8	1.368	0
HFC-125	CHF_2-CF_3	-95	N/A	N/A	N/A	0
HFC-134a	CH_2F-CF_3	-32	5.47	14.3	1.203	0
HCFC-141b	CH_3-CCl_2F	33	-0.3	1.2	1.231	6.4-15.1

N/A =Non Applicable, above Critical Temperature

Table 2. Product Applications of Carbon Dioxide, Nitrous Oxide, and Nitrogen

Carbon Dioxide
- *Hydroalcoholic disinfectant/deodorant sprays.*
- *Bug killers:*
  - *Ant and roach killers*
  - *Wasp and hornet killers*
- *Lubricants.*
- *Anti-statics, soil repellants, and wrinkle removers for textiles*

Nitrous Oxide
- *Whipped creams.*
- *Heavy-texture speciality foams.*
- *Windshield and car lock de-icer sprays.*
- *Furniture polish*

Nitrogen
- *Sterile saline solutions for rinsing contact lenses.*
- *Long-range, stream-type wasp and hornet killers.*
- *Injector-type engine cleaners.*
- *Over-pressurant for selected meter-sprayed vitamins and drugs.*

HCFC-123, HCFC-124, HCFC-125, and HFC-134a. The cost of HCFC and HFC propellants will probably be about 20 times that of purified hydrocarbons by 1993 or 1994, which may limit their application to relatively specialized products, such as metered perfume sprays in containers of 50 mL or less.

When flammable propellants are within the scope of company operations, isobutane and propane are currently the most reasonable choices. A "natural blend" consisting, for example, of 60% n-butane, 20% isobutane, and 20% propane can also be used.

Most U.S. aerosols are formulated to a pressure as low as is consistent with good operational performance across the anticipated temperature range of their use. Pressure limits for containers vary little between countries. In the U. S., the ordinary can holds product with pressures up to 2,067 kPa abs. (9.85 bar-gauge) at 54.4°C. Special cans with 14 and 28% higher pressure ratings are also available at extra cost.

The formulator must test the compatibility of the product with the dispenser and packaging systems to establish data on weight loss rates, can and valve compatibility, organoleptic stability, etc. Characteristics to look for include corrosion, demulsification, color

***Table 3.**, Exempted Excluded, or Nonregulated CFC Aerosol Products(U.S.)*

Mold release agents -- for molds making rubber and plastic items
Lubricants for use on electric or electronic equipment
Lubricants for rotary pill and tablet making presses
Solvent dusters, flushers, degreasers, and coatings for electric or electronic equipment
Meter-spray inhalant drugs:
a. Adrenergic bronchodilators
b. Cortico steroids
c. Vaso-constrictors - ergotamine tartrate type
Contraceptive vaginal foams - for human use
Mercaptan (as ethyl thiol) mine warning devices
Intruder audio-alarm system canisters - for house and car uses
Flying insect sprays:
a. For commercial food-handling areas
b. For commercial (international) aircraft - cabin sprays
c. For tobacco barns
d. For military uses
Military aircraft operational and maintenance uses
Diamond grit abrasive uses
For uses relating to national military preparedness
CFC-115 as a puffing (foaming) agent in certain food aerosols
Automobile tire inflators
Polyurethane foam aerosols
Chewing gum removers
Drain openers
Medical chillers - for localized operations
Medical solvents - as a spray bandage remover
Dusters for non-electric or - electronic uses - for phonograph records and computer tapes
Cleaners for microscope slides and related objects
Foam, whip, or mousse products in general
Small refill units for refrigeration or air-conditioning systems
All other 100% CFC product applications

or odor change, microbial proliferation, precipitation, clogged valves, and blistered dispenser lining. Thirty-six cans per variable should be test-packed and checked at 25 and 40°C, upright and inverted.

Aerosol Packaging Alternatives

The variety of alternative aerosol packaging forms available include bag-in-can types, such as the Sepro can, which separate the product from the propellant; piston cans; independent bag-in-can types; standard and aspirator pump sprays; pressurizing dispensers; and alternatives such as stick products. Various dispensing closures are also available.

Although several of these have been available for many years, they have not significantly penetrated the aerosol market for the following reasons:

- They generally cost more (finger-pumps and sticks are exceptions).
- They are limited in their product compatibility.
- They depend on chemical or mechanical (often manual) action to generate pressures needed to discharge the contents.
- Products must be delivered as very coarse streams, paste ribbons, or (sometimes) post-foaming gels--without having the broad range of the aerosol presentation.
- Sterility is generally impossible.
- Sprays can deteriorate during use.
- Several are incompletely tested,
- Several require capital expenditures for special filling or gassing equipment.
- Sizes are limited to the 3- to 12-fl.oz (119 to 355 mL) range. (Some are even more limited.)

Sales volumes are expected to gr however, taking some market share av from aerosols.

The Sepro can may be operated any position, since the bag is alw liquid-filled. As the product is used the bag collapses upward in a control way. Independent bag-in-can typ permanently separate propellant a product. In the simplest form, a pla pouch is inserted into an aerosol c before or after filling with concentrate.

The most common pump sprayer the finger-pump (as distinguished fr the trigger pump) sprayer. Aspirator-ty pump sprayers, such as the origi insecticide sprayers, are the o sprayers besides aerosols that c produce a space spray.

Pressurizing dispensers use pressure, the restorative pressure fr an expanded rubber bladder, or a sim arrangement, as the dispensing metho

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The complete report, entitled "Aerosol Industry Success in Reducing CFC Propellant Usage," (Order No. PB 90-143 447/AS (Cost: $31.00, subject to change) will be available only from:
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