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EPA **Project Summary**

Manual for Non-CFC Aerosol Packaging: Conversion from CFC to Hydrocarbon Propellants

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Because stratospheric ozone provides protection from biologically damaging ultraviolet-B radiation, and because chlorofluorocarbons (CFCs) have been strongly implicated in the thinning of the Earth's stratospheric ozone layer, there is an urgent need to eliminate production and use of the CFCs. In the U.S., CFCs were banned for use as propellants from nearly all aerosol products as early as 1978. In place of the CFC propellants, liquefied hydrocarbons such as propane, n-butane, and isobutane were found to be acceptable substitutes for the majority of aerosol products. This report provides technical assistance to aerosol product marketers and fillers in other nations now faced with eliminating CFCs under the terms of the Montreal Protocol. The report addresses the issues of hydrocarbon propellant supply, product reformulation, equipment conversion, and safety concerns for both the manufacturing plants and the aerosol products themselves.

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

Recent concern about depletion of the stratospheric ozone layer has focused on synthetic chemicals known as chlorofluorocarbons (CFCs). Scientists have concluded that destruction of the ozone layer by CFCs will allow too much harmful ultraviolet radiation to reach the Earth's surface, with potentially catastrophic results. The most serious consequences include a higher incidence of skin cancer and cataracts, suppression of the human immune system, damage to plant and animal life, and global warming.

In response to these concerns, countries around the world have agreed to phase out the production and use of CFCs by the year 2000. The Montreal Protocol, drafted under the auspices of the United Nations Environment Programme (UNEP), has been ratified as of October 1990 by 68 countries and the European Economic Community (EEC). Work is now underway to find substitutes and alternatives to replace CFCs, as well as to decrease CFC emissions in areas for which substitutes are currently unavailable.

Many alternatives exist for replacing the CFC-propelled aerosol package. This manual does not discuss the strengths and weaknesses of the many potential options. A brief list of the alternatives, however, follows:

- Hydrocarbon propellants;
- Other liquefied gas propellants such as dimethyl ether (DME);
- Compressed gas propellants such as carbon dioxide, nitrous oxide, and nitrogen;
- Hydrochlorofluorocarbons (HCFCs) such as HCFC-22, HCFC-123, and HCFC-142b;

- Hydrofluorocarbons (HFCs) such as HFC-152a and HFC-134a; and
- Non-aerosol packaging such as mechanical finger pumps, trigger sprayers, and other alternative packaging.

This manual provides manufacturers of aerosol products with the technical information that will enable them to convert from CFC propellants to hydrocarbon propellants. Hydrocarbon propellants are primarily mixtures (or pure components) of butane and propane, along with pentane, and to a much lesser extent, ethane.

For the reasons listed below, if manufacturers choose to continue to use aerosol dispensers instead of non-aerosol alternatives, hydrocarbon propellants are the most feasible near-term alternative to CFC aerosol propellants:

- Hydrocarbons can be treated and blended to obtain the physical and chemical properties that make them suitable aerosol propellants;
- Most hydrocarbons are essentially nontoxic, making them suitable for use in a variety of personal care and household products;
- Hydrocarbon propellants are less expensive than CFCs, enabling manufacturers to produce aerosols at a lower unit cost;
- Hydrocarbons are compatible with properly selected container materials and formulations, thus preserving shelf life and product stability; and
- Since the banning of CFC aerosol propellants, hydrocarbons have become the dominant aerosol propellant in many developed and developing countries and useful experience is available that can minimize the conversion cost for other countries.

Hydrocarbons also have two limitations or disadvantages:

- Hydrocarbon propellants are flammable; therefore, precautions must be taken by producers, distributors, and end-users to ensure that the aerosol products are handled safely.
- Hydrocarbon propellants belong in a class of compounds known as volatile organic compounds (VOCs), which are natural and synthetic compounds that contribute to the formation of what is known as photochemical "smog." In some urban areas where smog formation is a health and environmental problem, regulations have been proposed to reduce the amounts of VOCs in consumer products.

Properties and Availability of Hydrocarbon Propellants

A replacement aerosol propellant must have properties that allow the aerosol package to function: 1) the aerosol propellant must provide the pressure to expel the product from the container; 2) the propellant may serve as a solvent to aid in keeping the active ingredients in solution; and 3) the propellant must vaporize after leaving the container, producing a spray or foam. Other important properties of aerosol propellants are toxicity, stability, density and flammability. Table 1 compares the properties of the most common CFC propellants (CFC-11 and CFC-12) and the hydrocarbon propellants (isobutane, n-butane, and propane).

Either liquefied gases or compressed gases can provide pressure to expel product from the container. Hydrocarbon and CFC aerosol propellants are both *liquefied gases.* Throughout the life of the aerosol product, they generally provide a more uniform internal pressure.

The solubility of the propellant is important since it determines whether the overall contents are uniformly blended ("homogeneous"), or whether the contents exist in separate phases ("heterogeneous"). The hydrocarbon compounds are all nonpolar, which renders them insoluble with many polar solvents (including water). However, in some cases co-solvents such as ethanol can be used to provide single-phase blends of hydrocarbons, alcohol, and water.

The toxicity of propellants may be compared by using the threshold limit value (TLV, a trademark of the American Conference of Governmental Industrial Hygienists—ACGIH). The TLV is the maximum level of exposure for a person working 8 hours a day, 40 hours a week throughout a normal working career without adverse health effects. The occupational exposure guidelines for CFC-11, CFC-12, and hydrocarbon propellants are roughly comparable.

The corrosion properties of propellants may be compared by testing their hydrolytic stability. These tests measure the rate of hydrolysis (decomposition) in the presence of a steel test coupon in water. CFCs are generally less stable than the hydrocarbons. However, contaminants in "field-grade" hydrocarbons (water, and sulfur compounds) may have a major effect on corrosion.

No discussion of the properties of hydrocarbons would be complete without considering *flammability.* The flammability of an aerosol spray is a combined function of the composition of the product inside the container and of the design of the valve. Frequently, other major ingredients of the formula (e.g., alcohols or petroleum distillates) are also flammable.

Hydrocarbon propellants are derived from liquefied petroleum gases (LPGs) which come from the ground as constituents of wet natural gas or crude oil or as a by-product of petroleum refining. LPG usually refers to a mixture of propane and butane, although other hydrocarbons may also be present (ethane at the light end, and pentanes at the heavy end). The amount of LPG used for aerosol propellant is very small (less than 0.1% in the U.S. in 1981). Aerosol grade hydrocarbon propellants are prepared by first distilling the LPG to separate the various species. The distillation of hydrocarbon propellant is normally carried out at a specially designed plant that serves the regional aerosol industry. These plants are generally quite sophisticated and would be too large for any single aerosol filler.

Some aerosol products may use so-called "natural blend" LPG instead of distilled hydrocarbons. The primary advantage of natural blend LPG is that it is less expensive because there is less processing of the hydrocarbon. The natural blend propellant is suitable in products where odor is not as important (i.e., where the concentrate itself is quite odorous as in some degreasers or spray paints) or where the spray characteristics are not critical (such as wet sprays in some residual insecticides). A disadvantage of natural blend hydrocarbon propellant is that the quality varies, resulting in inconsistent pressure. Because the natural blend is produced by a coarse distillation, the amount of propane, butane, and pentanes may differ from one lot to the next, and this will affect the spray pattern. Natural blend propellants are likely to contain larger quantities of impurities (such as water, sulfurous compounds, olefins, or reactive particulates). The presence of water can be tolerated in water-based products, but not in products intended to be anhydrous.

Some types of aerosol products require a purer hydrocarbon propellant than other types. The most demanding aerosol products are aerosol perfumes and fragrances. Other products which require a highly refined hydrocarbon propellant include personal care products, food products, medicinal or pharmaceutical products, some household products, certain paints and coating sprays, and certain automotive and industrial sprays.

Before the propane and butanes are suitable for these aerosol propellant applications, they must be purified further to

Table 1. *Physical Properties of CFC and Hydrocarbon Propellants*

Name	Formula	Molecular Weight	Vapor Pressure @21°C (kPa)	Specific Gravity	Solubility in Water (Kauri-Butanol)	Toxicity (TLV)	Stability (g/L per year) (w/steel 30°C, 101.3 kPa)	Flammability (explosive range)
CFC-11	CCl_3F	137.4	89	1.476	60	1000	10	Nonflammable
CFC-12	CCl_2F_2	120.9	586	1.311	18	1000	0.8	Nonflammable
Propane	C_3H_8	44.1	855	0.5077	15.2	1000	—	Flammable (2.18 - 9.5 vol%)
Isobutane	C_4H_{10}	58.1	317	0.5631	17.5	800 (est.)	—	Flammable (1.86 - 8.5 vol%)
n-Butane	C_4H_{10}	58.1	221	0.5844	19.5	600	—	Flammable (1.86 - 8.5 vol%)

remove odorous and reactive compounds such as unsaturated hydrocarbons (for example, 1-butylene or propylene), as well as sulfur compounds and water. The processes used include: dehydration (for removing moisture); acid gas removal (for removing sulfur compounds); and sulfuric acid treatment or desiccant treatment (for removing unsaturated compounds). Contacts with industry experts and limited published data suggest that the most common type of hydrocarbon propellant purification is the solid adsorbent process. The solid adsorbent process can use such materials as silica gel, activated aluminas, or molecular sieve adsorbents for water or sulfur compounds (dehydration or acid gas removal). Unsaturated compounds can be removed using activated carbon or molecular sieves. The nonregenerable system is simpler and less expensive than a regenerable system, but the adsorbent(s) must be replaced periodically. The disadvantage of a non-regenerable adsorbent system is that, once the adsorbent becomes saturated, the impurities will no longer be removed, and contaminated propellant will enter the system.

An alternative to on-site purification is to use a central purification facility in conjunction with a distillation system. The central purification facility can operate with multiple beds that are alternated between purification and regeneration. Such a combined facility would comprise the basic elements of a regional hydrocarbon propellant supply.

Countries can import purified hydrocarbon propellant or LPG by overland or ocean shipment in bulk containers. Containers for shipping LPG include tank trucks, rail tank cars, and containerized pressure vessels (International Organization of Standardization containers) for ocean shipment.

Safety in Using Hydrocarbon Propellants

Hydrocarbon gases are used primarily as fuels. Because of their flammability, they must be handled with great care. In the U.S., the National Fire Protection Association (NFPA) has issued standards for manufacturing and storing aerosol products (NFPA Code 30B), and for storing and handling LPG (NFPA Code 58). In addition to these codes, which relate directly to the safety of aerosol products, many other NFPA codes are relevant. Important safety measures include:

- Locating manufacturing buildings and flammable propellant storage tanks at a safe distance [7.6 m (25 ft) or more] from the property fenceline and from other areas of the plant that could become sources of ignition or shrapnel.
- Providing for a blast wall between flammable propellant charging rooms and other areas.
- Providing a well-ventilated gas house that gives positive ventilation (at both normal and emergency rates).
- Routing all discharge vents from vacuum pumps, propellant pumps, and building ventilation systems no less than 3 m (10 ft) above the roof to ensure adequate dispersion.
- Complying with the 1990 U.S. National Electrical Code (NEC) for hazardous atmospheres, which requires that equipment be isolated so that these potential ignition sources are enclosed in "explosion proof" housings. The NEC Code specifies that approved fixtures be used on electric motors, switches, lamps, and other electrical equipment. The minimum ratings for the gas house and pump room where flammable hydrocarbon propellants are used are Class I, Division 1, Group D.
- Installing blowout walls or ceiling ("deflagration venting") to allow a controlled release of pressure if an explosion occurs. If venting is not possible or if personnel will be present when filling is underway, a specially engineered "explosion suppression" system is required. This type of system often employs pressurized halon, which is an ozone-depleting substance, and its production will be phased out under the Montreal Protocol.
- Providing automatic sensing systems to measure flammable gas concentrations in the gas house, sound alarms, and activate the emergency ventilation system and interlocks to cut off the propellant supply from the tank farm.

Again, this is only a partial list of the Code requirements. Other important areas cover such topics as fire sprinkler systems, standpipes, fire hoses, and fire extinguishers.

A fully enclosed gas house with two-speed ventilation and an explosion suppression system may not be necessary in warm climates, where an "open-air filling" area may be possible. The open-air filling technique has several advantages, such as reduced capital expenditures for installing or retrofitting an aerosol-filling plant.

In addition to the general safety considerations for hydrocarbon storage and building construction, other engineering safety measures apply to the hydrocarbon container valves and accessories, piping, and safety relief devices.

Labeling Requirements and Flammability Testing

Manufacturers normally place warnings on labels of aerosol products to ensure that the products are used safely and for their intended purposes. Among the most important labeling statements are the words FLAMMABLE and EXTREMELY FLAMMABLE. These warnings do not generally discourage purchases of useful products except on baby products, foods, and some pharmaceuticals.

In the U.S., two tests are used to determine when FLAMMABLE or EXTREMELY FLAMMABLE labels are required: 1) the Modified Flash Point Test, and 2) the Flame Projection/Flashback Test.

Equipment Conversion of Hydrocarbon Filling Operations

Automated Filling Lines

The large aerosol filling operation uses an automated production line that can produce 14,000 to 28,000 units per shift, which equals approximately 35 to 70 units per minute. The equipment that must be modified to convert from CFC aerosols includes the propellant supply, the gassing area, and possibly the main production area, depending on the location of the gassing area.

Automated filling lines typically use bulk storage of the hydrocarbon propellant. One of the most important guidelines is ensuring that the distance between the tanks and charging pumps and the production and gassing area meets the specifications in NFPA 30B. For tanks under 7.6 m^3 (268 ft^3), at least 8 m (25 ft) from the nearest production facility is recommended. For tanks over 7.6 m^3, at least 15 m (50 ft) is recommended. If existing fixed storage tanks are reused, they must be thoroughly cleaned (sandblasted) and hydrostatically tested at 2 times their maximum working pressure to ensure they can safely store the hydrocarbon propellant.

In addition to the storage area, modifications may be needed for the gassing and production areas. The gassing room should be constructed outside the main production area. The modifications required include increased ventilation, combustible gas detectors, isolation of electrical equipment in "explosion proof" housings, and possibly an explosion suppression system. The walls and roof of the gas house should be made blast proof, and blowout panels should be provided to allow a controlled release of pressure.

If a facility is not able to make the modifications suggested above, then an open-air gassing room may be an alternative. The main feature of the open-air gas house is the use of natural ventilation to keep any escaped hydrocarbon vapors below flammable or explosive limits. The gassing apparatus is located outside of the main production facility, with a solid roof, wire mesh walls on three sides, and a solid wall between the gassing area and the main production facility.

The costs for converting an automated aerosol filling line are difficult to estimate without site-specific details. One example is the Mexico Case Study, which estimated the cost to convert an automated filling line (producing 8 million cans per year) from CFCs to LPG to be $566,000 for capital investment (machinery and filling lines) and $793,000 for auxiliary equipment (gas detectors, fire extinguishing systems, and alarms), resulting in a conversion cost of $1.36 million U.S. dollars. However, the estimated propellant savings from using less expensive hydrocarbons in place of CFCs would be $1.69 million U.S. per year. Therefore, the cost savings from converting to hydrocarbons would more than offset the initial capital investment.

Manual Filling Lines

Small- to medium-sized aerosol-filling operations typically use a manual production line capable of producing 6,000 to 8,000 units per shift with two persons (limited to filling, gassing, crimping only), which would equate to approximately 15 units per minute. On the basis of one 8-hour shift per day and a 5-day work week, such a plant could conceivably produce nearly 2 million units per year. Other operations, such as labeling containers with paper labels or packing, would either slow the rate or require additional labor.

A typical manual aerosol filling line uses air-operated and manually actuated equipment. Each container must be transferred manually from one step to the next. Cold filling is *not* appropriate with hydrocarbon propellants and should be replaced by pressure filling. A single-station pressure filling machine may cost up to $30,000.

Required equipment modifications would typically be limited to the propellant supply and the gassing area. The hydrocarbon storage used for small manual filling lines are typically several 53-kg (117-lb) cylinders manifolded together or a 385-kg (849-lb) container. Cylinders not in use should be stored in the open air or in well-ventilated areas. No more than six cylinders should be stored together with a minimum distance of 3 m (10 ft) between the storage and a boundary, building, or fixed ignition source (such as pumps, electrical motors, or vehicles). All cylinders should be stored upright, with protective valve caps in place, and securely chained.

In addition to the propellant supply, equipment modifications for manual lines must be made to the gassing area. Many small filling operations are located in crowded urban areas, and the use of an open-air gassing area would not be possible. One way to significantly reduce the hazards associated with hydrocarbon propellants would be to locate the gassing and crimping operations within a laboratory fume hood. These types of hoods have been successfully used for laboratory-scale, manual filling operations that closely correspond to cottage-size production facilities.

The exhaust from the fume hood should be connected to a flue or pipe duct that uses an explosion-proof fan motor. The end of the duct or piping should exit directly through the roof of a one-story building or to an adjacent outside wall if the filling room is located in a multi-story building. The location of any ignition sources that may be near the exhaust duct should be considered. The fume hood, fan-motor, and any equipment used within the fume hood (such as lighting) should be Class I, Division 1, Group D explosion-proof equipment.

The costs for converting a manual aerosol filling line are also difficult to estimate without site-specific details. The estimated cost to convert a hypothetical manual filling line (producing 500,000 cans per year) from CFCs to LPG is at least $12,000 U.S. dollars. This includes purchase of explosion-proof motors, starters, and solenoid valves; installation of explosion-proof fume hoods for gassing equipment and test baths; and construction of a covered, fenced hydrocarbon storage area. This initial capital investment would be more than recovered by the material cost savings of using hydrocarbon propellants instead of CFC propellants.

Aerosol Product Storage

Since hydrocarbon propellants are flammable (containing butane, propane, or a mixture of these two, or less frequently, pentane or ethane), producers, distributors, and end users must take extra care to handle them safely. Aerosol products can be classified into three levels according to their perceived flammability hazard. The classification considers the percentage of flammable base material and flammable propellant. Materials that mix with water, such as ethanol, isopropanol, propylene glycol, and acetone, would dissolve in the water from sprinklers and fire hoses during a fire and be rendered nonflammable. Water immiscible materials, on the other hand, such as toluene and aliphatic petroleum distillates would not dissolve and could spread as a burning top layer as water was directed at a fire.

Level 1 aerosol products are those whose base products contain up to 25% by weight of materials with flash points of 260°C (500°F) or less. Level 1 aerosol products do not require special fire protection measures. These "water-based" aerosol products may be stored as a Class III commodity as defined in NFPA Standard 231 for Rack Storage of Materials; i.e., equivalent to paper, cardboard, and wood products.

Level 2 products are those whose base product contains either 1) more than 25% by weight of water miscible materials with flash points of 260°C (500°F) or less, or 2) more than 25% but less than 55% of water immiscible materials with flash points of 260°C (500°F) or less. Level 3 products are those whose base product contains more than 55% of water miscible materials with flash points of 260°C (500°F) or less, *or* the flammable propellant equals or exceeds 80% of the net container weight.

Level 2 and Level 3 aerosol products may be stored in a general purpose warehouse that either has no sprinklers or is not protected in accordance with NFPA 30B, but the quantity is limited to 1135 kg (2,500 lb). Storage of greater amounts of Level 2 and Level 3 aerosol products in general purpose warehouses requires compliance with the protection guidelines for automatic sprinklers and palletized, solid pile, or rack storage arrangements as listed in NFPA 30B.

Aerosol storage in sales display areas and backstock storage areas is also addressed in NFPA 30B.

Product Reformulation

The characteristics of hydrocarbon propellants as they relate to formulations and performance are discussed. Dispersion, one major attribute of aerosol propellants, is the efficiency with which a propellant can produce a fine spray or acceptable foam. The dispersive effect is not linear but is modified by vapor pressure and solubility factors. It normally can be used as a general guideline to determine equivalencies when changing from one propellant to another.

After a concentrate has been tentatively developed, the correct type and amount of propellant must be added, and an aerosol valve must be used that will develop the desired spray pattern or foam puff. One of the most important characteristics that the formulator looks for is particle size distribution. There are several techniques to decrease the droplet size if it is too coarse. One approach is to use a vapor-tap valve.

Approximately 40-50% of the world's 8 billion aerosol products use vapor-tap valves. Such valves have an orifice extending through the side or bottom wall of the valve body and into the head space area. The orifice may be enlarged to decrease particle size. However, this has several negative effects.

To devise a good aerosol product, a formulator must minimize the risks of flammability and possible explosivity. It is a tribute to the excellence of the aerosol packaging form that extremely flammable products can be safely dispensed, if the user follows label directions, and if the formulator is able to make allowances for reasonably foreseeable consumer misuse.

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. For example, hair sprays are expected to work well between 13°C and 37°C, and reasonably well just outside these limits.

The formulator's job is not complete when an acceptable product and packaging system have been developed. Test packing is always needed to establish data on weight loss rates, can and valve compatibility, etc. Several options are discussed to correct corrosion problems, such as addition of corrosion inhibitors, increasing the pH, or minimizing the presence of chloride ion.

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The complete report, entitled "Manual for Non-CFC Aerosol Packaging: Conversion from CFC to Hydrocarbon Propellants," (Order No. PB92-101344/AS; Cost: $35.00, subject to change) will be available only from:
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