



SAFETY FIRST:

TECHNICAL GUIDE FOR  
THE SAFE HANDLING  
OF HYDROCARBON  
PROPELLANTS



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Cover photo: © UNEP DTIE OzonAction Programme, 1999. M. Haddad & Sons Co., the largest aerosol manufacturing plant in Jordan that was successfully converted to HAPs with financial support from the Multilateral Fund and assistance from the World Bank (JOR/ARS/07/INV/14).

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## Preface

“Sustainability needs safety”



***The end of chlorofluorocarbons (CFCs) is not in question, it is only a matter of time.***

The global phase out of CFCs is in an advanced stage under the Montreal Protocol, including among industries that manufacture aerosol products. The remaining CFC consumption for aerosols in developing countries has been estimated to be around 4,300 tonnes in 2001, which represents a dramatic 71% reduction compared to the sector’s CFC consumption in 1997. CFCs are a small and ever-diminishing share of propellants – less than 1% of the total – and hydrocarbon aerosol propellants (HAPs) have filled the gap with astonishing speed to become the principal replacements.

**Why then this guide when the CFC phase out is so far along?** Because the issue of safety related to HAP propellants, particularly for small and medium-scale enterprises (SMEs), is now at the forefront – Safety is indeed First. The Aerosols Technical Options Committee (ATOC) of UNEP Technology & Economic Assessment Panel has stressed that in the process of replacing CFCs in the aerosol industry of developing countries, every effort should be directed to ensure that safety standards at the manufacturing plant and at the consumer level are maintained. To meet this goal, the ATOC recommended among other things that good manufacturing practices, technical information about new propellants, and proper installation guidelines should be made available and distributed as widely as possible. The ATOC also noted that despite increased progress, one of the remaining problem areas is the conversion of small and very small CFC users. Safety is an area where SMEs often fall short and they need continuing support to make a smooth transition to HAPs.

This guide helps respond to these needs. The sooner that the safety and small users issues are addressed, the faster that total phase out in the aerosol sector will be accomplished. **Putting safety first ensures the long-term sustainability of the phase out.** While CFCs will soon be a phase out success story under the Montreal Protocol, we must ensure that HAPs become a “phase-in” success by helping that lives, livelihoods, and the environment are protected at the same time.

This guide was developed by the UNEP DTIE OzonAction Programme as part of UNEP’s work programme under the Multilateral Fund for the Implementation of the Montreal Protocol. It is unique in that it is the first safety-related document produced under the Fund, and it was written by industry experts of international renown for use by industry practitioners in real companies. Safety First is thus a first in many senses of the word.

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## Summary

This publication is designed to provide technical assistance to those aerosol fillers who use hydrocarbon propellants in the production of aerosols. It describes the many safety measures that must be taken to prevent these dangerous propellants from causing fires or explosions. Although propane, the butanes, and their mixtures have been used to pressurize aerosols since 1954, there are still periodic reports where aerosol plants and warehouses have suffered terrible fires, sometimes with loss of lives. Worldwide, the fire losses have now exceeded about US\$ 1,600,000,000.

The largest aerosol plants in South Africa and Algeria have burned to the ground. The second largest aerosol plant in the USA burned down completely. After it was rebuilt, it suffered two more major fires and a gas-house explosion. The second largest aerosol filling plant in Canada also burned down. Some of these events are shown in pictures provided in this guide.

There can be no complacency or relaxation of safety when dealing with hydrocarbon gases. In a sense, they can be regarded as potential killers, locked up inside tanks, pipes and even aerosol cans. If they escape in sufficient amounts (and find an ignition source), serious fires or explosions will result, and plant workers may be badly burned or killed. Afterward, plant reconstruction costs always exceed any insurance coverage, business interruptions can be disastrous, and future insurance costs will increase dramatically. Some businesses never recover from serious fires or explosions. The main purpose of this guide is to prevent such occurrences.

We will cover here the **theoretical** aspects of flammability only as they directly relate to plant safety. The importance of **ventilation** and **air-flow** will be highlighted, as well as the crucial need to avoid **ignition sources**. Safe design and construction of **gassing rooms** will occupy a prominent place in Section # 1. **Storage tanks, piping**, and other plant and engineering aspects of safety will also be discussed.

Safety training and related factors is also dealt with here, as many of the accidents that have occurred over the years were due to human errors.

A second major consideration of this guide book is the bad odor of almost all raw hydrocarbon gases. This means that finished aerosols can have very unpleasant odors, negatively affecting sales.

Fillers in such countries as Lebanon, Indonesia, Vietnam, and a few in South America do some importing of highly purified (Aerosol Grade) hydrocarbon gases from North America and Europe. This is costly and may involve government approval, uncertainties and delays. A more favored approach is to remove the impurities with the most offensive odor, by absorbing them in specially prepared zeolyte (or sieve) pellets. The pellets are contained in a device called a Molecular Sieve – or “MolSiv”. Some of the impurities, called unsaturates or olefins, cannot be captured by absorption. The odor of the product is almost always improved by the removal of sulfur compounds to the extent that the hydrocarbons can be used in aerosols, without receiving consumer complaints.

Because of a lack of technical information, there is a large amount of confusion and uncertainty regarding the specifications and operation of MolSiv equipment. This guide will attempt to provide the necessary information.

Finally, aerosol formulations based on the use of hydrocarbon propellants will often be quite different than those that used the CFC propellants. For example, water can now be used very efficiently, for aerosols such as insect sprays, air fresheners and cleaning products. Water also reduces the flammable potential of these products, and lowers the cost of the formulas. A number of modern aerosol formulas will be provided, with packaging specifications, as a useful guide for firms wishing to take maximum advantage of the hydrocarbon propellants.

# Technical aspects of hydrocarbon gas Flammability

## INTRODUCTION

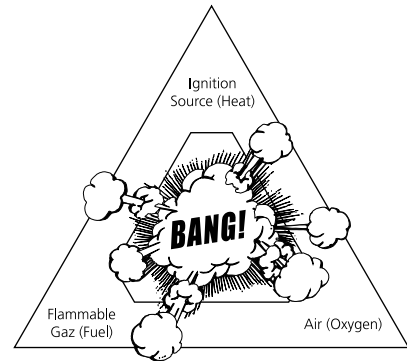
In 2002 the world production of aerosols was almost exactly 11,000,000,000 units. Over 80% of these aerosols used hydrocarbon gases as the propellant. In many countries the hydrocarbons were the only propellants available. There are three of these gases: propane (high pressure), isobutane (medium pressure) and n.butane (low pressure). Gas wells and oil refineries produce various blends of these three gases. Blends have different pressures, according to their composition. The aerosol fillers must generally adjust their formulations to use whatever blend is domestically available. In some countries the composition of the mixture may change during the year, as refineries make adjustments to handle the variable requirements of other industries.

All the hydrocarbon propellants are shipped and stored as the pressurized liquid, in tanks or cylinders. The raw, or unrefined products are called "Liquefied Petroleum Gases," or LPGs, and they almost always have bad odors. There are two main sources of this bad odor: sulfur compounds and unsaturated hydrocarbons. The sulfur compounds are best removed by using a molecular sieve unit. When properly set up and maintained, the molecular sieve zeolyte pellets will absorb the sulfur compounds very effectively. This removes most of the bad odor. The unsaturated hydrocarbons (olefins) cannot be removed, except by using extremely expensive and complicated equipment. So they must be tolerated. Hydrocarbon propellants, purified by molecular sieving, are called "Hydrocarbon Aerosol Propellants," or HAPs. As the name indicates, they are suitable for use as aerosol propellants. The odor of these HAP gases will vary, according to the concentration of unsaturated hydrocarbons in the original LPG. In a few locations the HAPs will be so low in unsaturated hydrocarbons that even the concentrated gas will be almost odorless. But in other places the unsaturated hydrocarbons may be as high as about 1 to 5%, and this gives the HAP sufficient "gasoline type" odor that it is not well-suited for use as the propellant for aerosol colognes and a few other products. Because of this, in some places blends that have over 0.1 % (1000 ppm) unsaturates are denied the name "HAP."

Propane, isobutane and n.butane are all extremely flammable. Even at very low concentrations in air they are easily ignited by flames or sparks. Very large fires may then occur, and if the ignition takes place inside a closed room or building, then an explosion will happen. Workers may be seriously injured or killed, and the building will often burn down. Some companies cannot stand such terrible losses, and they may go out of business. The main purpose of this safety manual is to help protect factory workers from fires and explosions, to keep them from being badly burned, to save their jobs, and to prevent factories from being destroyed.

## TECHNICAL ASPECTS

Hydrocarbon propellants will chemically react with the oxygen in the air, if they escape from tanks, pipes, pumps and gassers, and can find a flame, spark or other ignition source. To ignite, the concentration in air must be within the flammable range – about 2% to 9% by volume of the gas in air. As an example, if as little as 18ml of liquid isobutane is poured into a 200 liter open-top steel drum, it will produce about 4.120 liters of gas. If this gas is mixed with the air in the drum, it will be present at 2.06% by volume. This is inside the flammable range, and if a lighted match is thrown into the drum, the entire contents will instantly catch fire, producing flames about 2 meters high. If the test is repeated, now using a drum with a steel top, touching a match to the small hole in the top will cause a serious explosion, possibly killing anyone standing next to it.



Some engineers are familiar with the concept of a “Fire Triangle.” This shows that three things are necessary for a fire or explosion: air (oxygen), fuel, and an ignition source. The air is always present. The fuel can be the hydrocarbon propellant gases, if they are within their flammable range in air. And the ignition source is either a flame or a spark. Electrical, static or mechanical sparks are the most common source for aerosol plant fires. When these three conditions are present, a fire will always result. If the fire is large, and confined inside a room or building, there will also be an explosion.

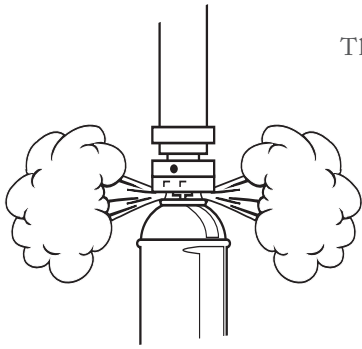
The hydrocarbon propellants are flammable in air when they are present in concentrations of from 1.5 to 9.5%. Above the upper explosive limit (UEL), there is too much fuel and not enough oxygen to burn. The UEL of hydrocarbon flammability in air is of no import here, but to reach and exceed it in a given place probably means that a lesser concentration exists nearby, and therefore a dangerous situation exists. For flammable gases, the lowest concentration in air that can burn is called the LEL or Lower Explosion Limit. Sometimes it is called the LFL or Lower Flammability Limit. For the hydrocarbon propellants, this value is about 2.0% by volume in air.

**Table #1: Flammable Limits in Air (the lower figure is the LEL):**

Substance:	Limits of Flammability:
Propane	2.2% a 9.5%
Isobutane	1.8% a 8.4%
N-butane	1.8% a 8.5%

In practice, this concept can sometimes be misleading. It assumes complete mixing of gas and air, which almost never happens. For example, if only 1 ml. (0.56 gram) of liquid isobutane is poured into the 200 liter drum, it would immediately evaporate, producing flammable gas at the bottom area of the drum. If a lighted match is then thrown into the drum, a fire with a flame volume of about 20 liters would result.

All three hydrocarbon gases are heavier than air. Isobutane and n-butane are over twice as heavy as air. When these gases escape from a leak or from a gasser head, they will normally fall rather quickly to the floor and then spread. There is generally some air movement, and most of the spreading will occur in the same direction as the airflow. In one plant, leaking isobutene vapors traveled over 20 meters, across the floor to an electrical ignition source. The fire killed 4 people, injured 16 more, and burned down half the plant.



There is always routine HAPs leakage during the gassing operation, often between 2 and 3 mL per can.

Some propellant leakages start very small and gradually get larger and more dangerous. This is especially true for gassers, which always leak somewhat, as rubber sealing gaskets gradually wear out or springs can weaken where springs are used. Leakage sites can often be detected by moisture condensation, since the evaporation of leaking hydrocarbon will cool that location. Very serious leakages will chill the area so greatly that the condensed moisture from the air will turn into ice. These leakages must be corrected without delay, especially if they occur inside a building.

Leaks can also be detected by the hydrocarbon odor, if there is very little air movement from wind or ventilation. LPGs have more odor and their concentrated vapors can be detected more easily than the HAPs. Smelling is best done at the floor level. Periodic examinations of propellant pipe and hose connections, of valves, and other equipment can be made with "Explosimeters," if available, or by brushing on a thin layer of detergent solution, if they are not. The soap solution will produce gas bubbles at any point of leakage. Some facilities may have gas-sensing equipment that is permanently installed. This is designed to determine if excessive gas leakage is occurring in sensitive areas, such as gasser enclosures or gassing houses. As a rule, two gas sensing heads are mounted near the floor and will read gas concentrations as "%LEL." An alarm will indicate excessive gas levels. These complex devices are very useful, but cannot be used to check for gas leakages outside the areas monitored by the sensing probes.

**Adequate ventilation is the most important protection against dangerous flammable gas accumulations.** Outside the plant, the natural ventilation from air movement provides almost complete protection, if the air is able to circulate freely. For example, open-air gassing is considered to be very safe. In those situations where buildings, walls or tanks interfere with good air movement, the use of large electric fans is recommended. Typically, they are located about 3 meters high and aimed at the gasser or other equipment from the same direction as the prevailing wind. They do not need to be turned on during days when there is good natural air movement. Many are not explosion-proof, but the wires are always properly protected in conduit, and the "on/off" switch is far from the gassing area.

Bringing pipelines of liquid hydrocarbon propellant inside the plant is not generally recommended. If it is done, the installation should be as simple and short as possible and used only to supply the gassing machine. Molecular sieve equipment, propellant pumps, gas cylinders and so forth should be kept outside the plant. Mechanical ventilation must be used to safely exhaust the released propellant gas to some point outside the building. Ideally, air is provided by fan-motors and enters the controlled area through registers placed at about floor level. It sweeps along the floor, carrying the heavy propellant vapors with it, until it passes to the outside, via more floor-level registers. The special ventilation requirements for inside and outside gashouses will be described later.



There is a solid ring of ice on this gassing adapter. This is dangerous leakage. The machine should be stopped and the seals changed.

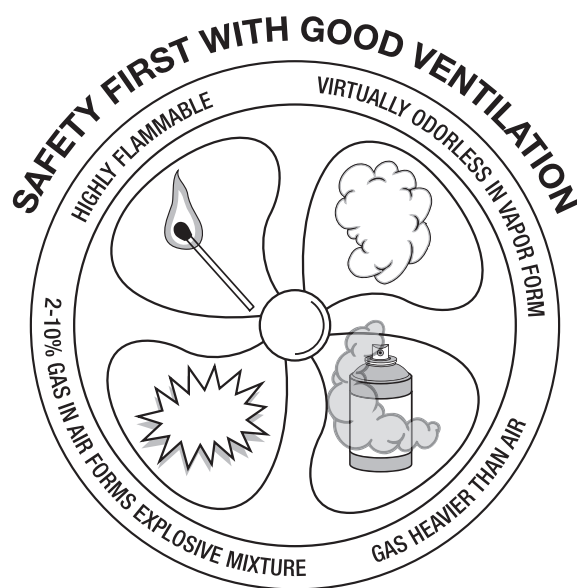


Filled aerosols may very slowly leak in warehouses. The leakage is only about 1 to 6 grams per year, unless the can, valve, or crimped seal is defective. Still, many thousands of aerosol cans should not be stored in a closed warehouse area. The natural ventilation from opened windows or doors is sometimes used, but floor vents (screened to keep out rodents) are preferred. In at least one case, hydrocarbon propellant vapors accumulated in a corner, behind pallet-loads of filled aerosols, and finally caught fire from an electrical spark. The building was destroyed. In another plant, vapors released from filled aerosols slowly drifted down into a basement room and slowly accumulated there until they exploded from contact with the pilot light of the furnace.

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Good ventilation is the first and most important defense against hydrocarbon propellant flammability. It is a major consideration in the protection of lives and property. The mere opening of plant doors is no substitute for good mechanical ventilations.

This «safety fan» indicates the principal concerns that require ventilation.



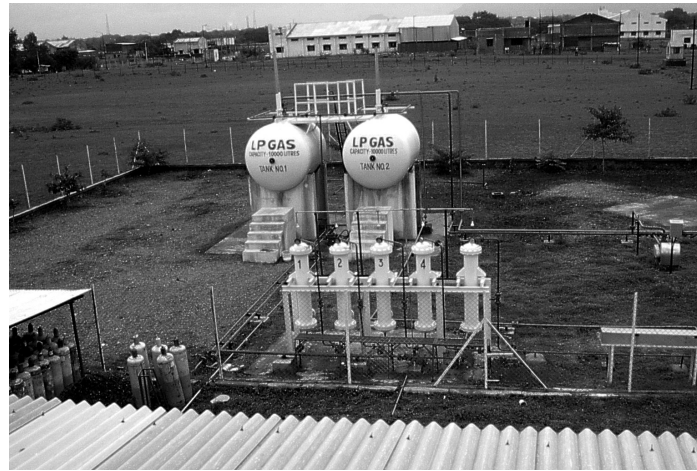
## ENGINEERING ASPECTS

### General Considerations

Bulk-tanks and cylinders of flammable gases should always be located outside. Cylinders (both empty and full) may be stored in a separate small building, if these are well ventilated by openings near the floor level. In warm climate countries, a fenced shed is more effective. Local regulations may direct that bulk tanks be located at certain distances from building, property lines and tanks of flammable liquids. The usual minimum is 8 meters. In some countries the bulk-tanks must not be aimed at any nearby building. The bulk-tank area must be kept free of other things, such as drums, wood pallets and spare parts. Ample room and strong barriers must be allocated for the safe arrival, unloading and departure of LPG tank-trucks.

Propellant pipes, hoses, pumps, filters, molecular sieves, valves and similar equipment must be located above the ground and outside whenever possible. They must be kept away from the paths of moving vehicles, such as tank-trucks and plant lift-trucks. Pipe supports must be installed at reasonable intervals. If a propellant pipeline must cross over a road, it must be high enough to remain clear of any vehicle. Special crossbeam support will be necessary, to prevent sagging and possible breakage. In areas of vehicle traffic, support beams must be protected by heavy reinforced concrete barriers.

The LPG storage area should be on hard ground, reasonably flat, and protected from plant growth by laying heavy polyethylene film over the ground and placing an 80 to 100mm thick layer of gravel over the film. The area should be surrounded by a wall or fence, at least 2m high, with a single or double gate for tank-truck unloading. Ideally, bulk-tanks should be mounted on two saddles of reinforced concrete. In rare instances, bulk-tanks may be installed underground, provided special precautions are taken to prevent corrosion, which could eventually lead to catastrophic leakage.



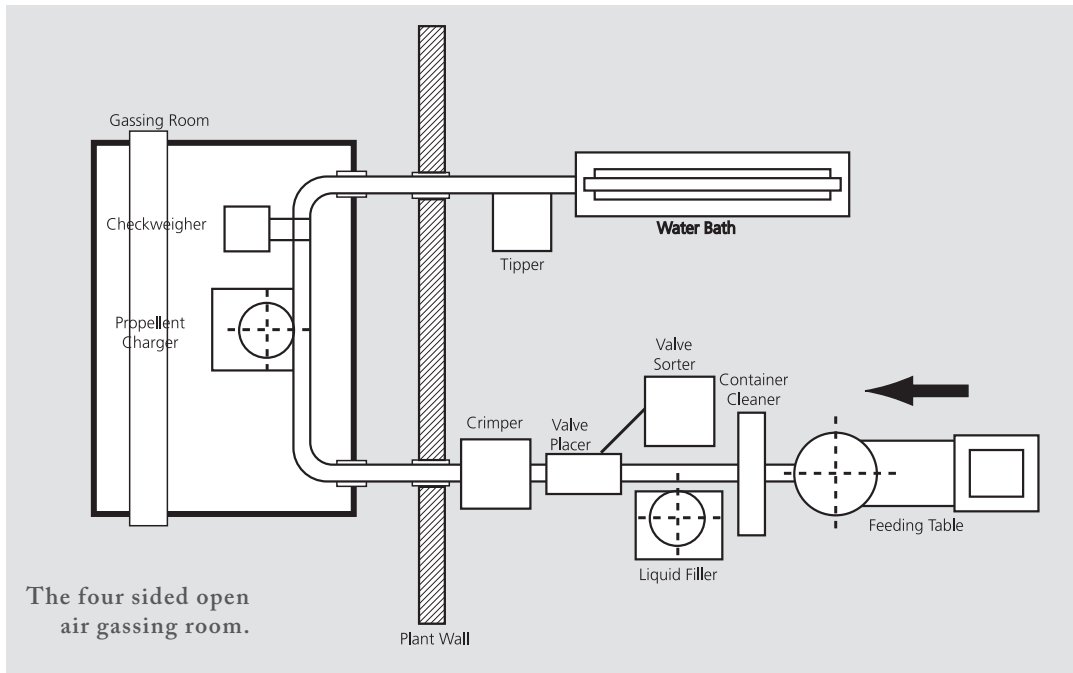
A good small tank farm in India



A somewhat larger tank farm, also in India

Outside gassing areas are strongly recommended. In warm climates simple hand-operated or semi-automatic gassers can be installed, at least 4m from the main plant, and under a roof that will deflect the rain. Gassers are also available that are enclosed within small metal boxes, having two or three access doors. Since all gassers release propellant gas while operating, these boxes should come with a mechanical air exhaust system.

There are several possible layouts of outside "open air" gassing facilities. In the best of these, all four walls are completely open, possible "walled" with chain link fencing. In Example # 1 the company has installed canvas "walls" hanging loosely from the roof, to stop rain from entering this under-sized room. The canvas "wall" must stop one meter above ground level, so that it will not hinder air circulation thus defeating the purpose of 'open air' concept. In Example # 2 the room is much larger and because it is on a property where there is no danger of theft, it has no walls at all. In both cases filling and crimping are done elsewhere and cans are sent outside for gassing on trolleys.

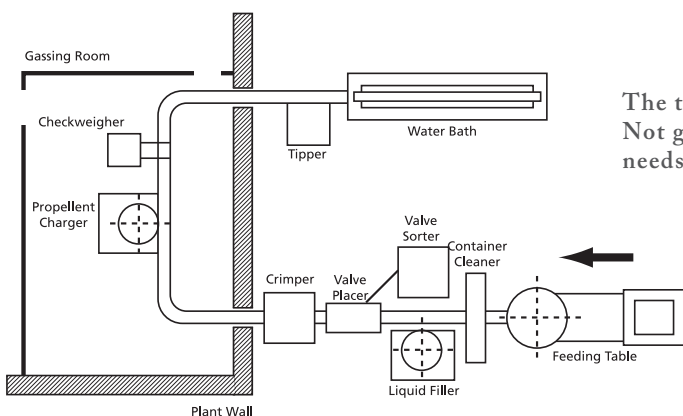
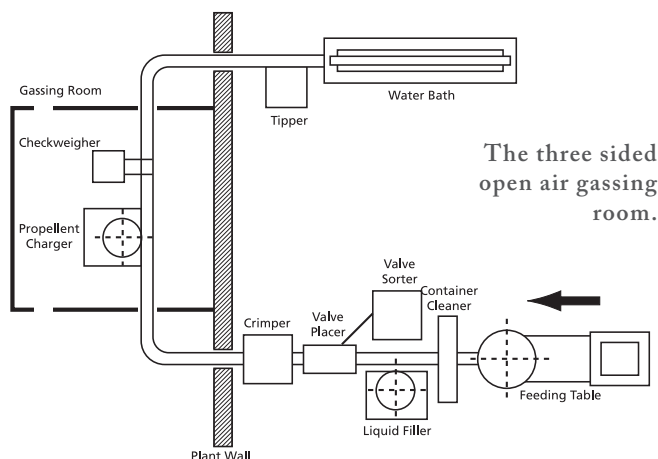


Example # 1:  
an undersized open air gassing room.

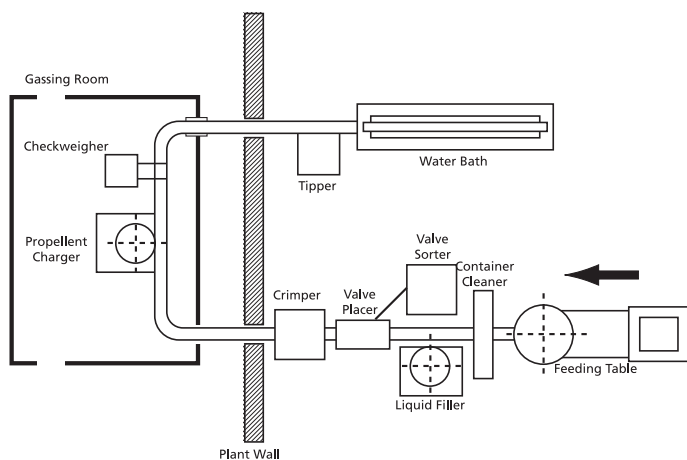


Example # 2:  
a completely open gassing facility.

Some companies install open air gassing facilities against the wall of the factory – these are thus three sided open air gassing facilities. In this case, it is necessary for gassing to take place at least 3 and preferably 4 meters or more from any holes in the wall, or explosion proof fans can be used to blow air as a barrier so that leaked gas cannot enter the main plant. There are also a few two sided open air gassing rooms, these must always use fans to avoid LPG from accumulating, and also from passing flammable vapors into the main plant.



If inside gassing facilities must be used, the gasser must either be positioned in a small metal box with good internal ventilation, or in a small gashouse, typically about 3 x 4 x 4m high, with good ventilation at the floor level. The exhaust ductwork must lead to a discharge point outside the building. Gassers that work reliably, without the presence of an operator, can be engineered and purchased.



The layout of the outside enclosed gassing room is the same as with a four sided open air gassing room.

Inside production equipment layouts can take many shapes, but are often in the shape of a "U", with the gasser in the middle area. Essential equipment will include the product filler, crimper, gasser and hot water bath. Other equipment may include an automatic valve inserter, conveyors, coders, can counters, and so forth. Some inside gassers are made as a part of rotary filler/crimper/gasser machines. If the line includes an outside gasser, the filled and crimped cans are conveyed to a point at least 2m outside the main building, where they enter the gasser. Once gassed, they are conveyed back inside the building and usually directly into the hot water bath. The inside production area should be ventilated and located well away from the finished product warehouse area.



## Safety Considerations

Potentially flammable and explosive hydrocarbon gases can enter the plant building from normal gassing operations (about 2 to 3ml. of liquid leak per can filled) or from leakages at pipe joints, pumps and other equipment. Sometimes there will be very dangerous gas leaks, due to hose failures or pipe breakages. Good ventilation is the first and most important defense against gas accumulations.

Outside gassers are mostly ventilated by wind action, often supplemented by large fans. Outside gassers, within metal boxes, almost always contain a ventilation system for the enclosure itself. If these same gassers are used indoors, the emitted gas-air mixture must be captured by metal ductwork and transported to an outside location. Otherwise, the boxed gasser ventilation system is of no value, and is actually dangerous.



These outside gashouses were constructed by an aerosol filler to the specifications indicated in this manual.

Gassing equipment is very often placed outside in a highly protected room called a gashouse. These structures are made of metal and concrete with ventilation equipment often placed on the roof. Incoming air will enter through registers all along the longer wall, placed at or near the floor level. It will move along the floor, sweeping it free of heavy HAP vapors, and entering a long row of registers at floor level on the opposite long wall. In turn, these will direct the gas-air mixture into a metal duct system that releases it into the air at a height of at least 5m.

The ventilation rate is very important. It can be calculated by making certain assumptions as to safety factor (usually 20%) and the %LEL at equilibrium (normally 8 to 10%). For example, if the gasser releases 1.5ml. of liquid HAP per can and is running at 37 cans per minute, then the calculated exhaust rate will be 500 cubic meters per hour. The fan motor of the exhaust system should be established by considering the maximum anticipated gas release rate.

Make-up air can enter, mainly through the openings at the base of one long wall and partly through the wall openings that let cans be conveyed into the gashouse, and then back out. These openings must be large enough to let sufficient air enter that a severe negative pressure will not occur, causing a strain on the exhaust system. A slight negative pressure is desirable. In more sophisticated ventilation systems, the makeup air is mechanically provided and engineered to be about 95% of the exhausted air volume. This gives the desired slight negative pressure in the gashouse.

The ventilation air should flow evenly across the entire floor area. Workbenches, drums or other things that block this smooth flow should be minimized. The doors must be kept closed. Floor drains, sumps, channels or other holes in the floor tend to collect and concentrate heavy gas vapors and should be eliminated. The fact that HAPs is much heavier than air must always be remembered.

**Table # 2: Weight of HAPs Vapors (the weight of air = 1.0):**

Substance:	Weight as Vapor:
Air	1.0
Propane	1.55
Isobutane	2.01
N-butane	2.08

The best gashouses have a two-speed ventilation system. This is electrically connected to a %LEL sensing device. When due to an abnormal situation, the sensors detect a 20% LEL concentration, the standard ventilation rate will automatically change to the emergency rate, which is typically three times as fast. (or 1500 cubic meters per minute in the example). At the same time, an alarm will be energized, such as a horn or yellow blinking light.

These ventilation requirements apply equally to inside gassing rooms, since now the safety of many workers and the main building may be affected. It is necessary to carry the gas-air exhaust mixture to the outside through metal ducts that go either through the plant roof or through a wall.



This small gassing room in Tunisia has only one exhaust stack, but two speed extraction.

If the ventilation system fails, production must stop immediately. In the example of a 1.5ml. of liquid propellant loss per can, at 37 cans per minute, 56ml. of liquid would be released every minute. For isobutane, this would produce 12.8 liters of pure gas or 0.712 cubic meter of the flammable LEL mixture with air. After only a few minutes, if ignited, this would be enough to explode a small size gashouse.

Ventilation of other production equipment is important. The hot water bath can seriously overheat and explode cans if it stops from a power failure or conveyor chain break – or if the thermostat malfunctions. Floating cans may also be overheated if they are near the hot water inlet. If a sufficient number of cans rupture, dangerous amounts of HAP will be released. Also, those cans found to leak in the hot water bath are normally collected in a drum, near the end of the bath. They can easily fill up the drum with flammable gas, which will then spill over the top (invisibly) and spread across the floor. The drum can be emptied outside at reasonable intervals, but a better solution is to install an exhaust system over the hot water batch and then have a small, flexible duct, going to the bottom of the drum, to constantly remove any released HAP vapors. The collection drum would best be grounded.

The slow speed floor level ventilation of the production area, with air traveling at about 300mm per minute, will remove any vapors from leaking propellant lines to the gasser, from conveyor jams that could result in puncturing cans, from heat-shrinking tunnels (used to apply some labels), from lift truck propane tanks and from the application of actuators and foam spouts to aerosol cans. If the production area is reasonably open to outside air movements, this general ventilation may not be needed.

Cross-ventilation through open doors, during working hours, is generally sufficient to remove the vapors emitted at extremely slow rates from thousands of filled cans, from any cans perforated by severe corrosion,

and from cans that may be perforated or crushed by lift trucks. A number of warehouse fires have been caused by the dropping of fragile containers of very flammable liquids, such as paint thinners. If these burst and spill the liquid, it may catch fire and cause nearby aerosols to heat up and explode. The usual result is that the entire warehouse and the contents will be lost. Some of these fires have burned for as long as 8 days, at costs of over US\$ 100,000,000.

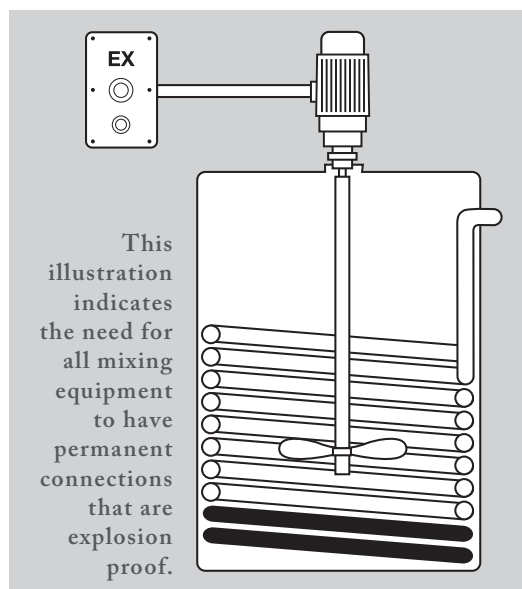
Ventilation of the empty goods warehouse (cans, valves, caps, corrugate, cartons, etc.) is generally not necessary. In one warehouse, two workers were smoking in such an area, and stacks of corrugate cartons caught fire from a match or a spark. They produced a very dense cloud of smoke. Firefighters could not see through this smoke and some were hospitalized from breathing too much of it. The plant was saved from destruction, but there was still considerable damage.

The chemical warehouse should have moderate ventilation, usually from wall registers that allow wind currents to flow through the area. Some plants make a practice of storing extremely flammable and volatile liquids (like pentanes) outside the plant, but also away from direct sunlight. The inside storage area should be inspected each day for any sign of leakage or chemical vapor accumulations.

All compounding areas should be well-ventilated. Solvents such as ethanol, isopropanol and especially acetone, are volatile and can produce flammable vapors. The hazard level increases during hot weather. Pentane and hexane vapors are extremely dangerous. The vapors are up to three times as heavy as air, and their LEL is 1.2 to 1.4% by volume. If there is some wind motion, opening large doors will be adequate. Otherwise, large-capacity mechanical ventilation, with intakes near the floor, will be needed. Sources of ignition must be rigorously excluded from compounding areas and all electrical equipment must be explosion-proof. A number of serious fires have started in these areas, usually from sparks. Aerosol plants in Canada, South Africa and India have been totally destroyed from solvent fires in the compounding or filling areas.

Many empty compounding and storage tanks will be filled with potentially flammable solvent vapors. If workers go into these tanks they may die from harmful vapors, or from a lack of oxygen. The vapors must be removed, via the bottom outlet, and discharged outside the plant before cleaning. This should be part of good house keeping rules. Electrical grounding of compounding vessels is very important, as there have been incidents where the vapor caught fire for no apparent reason.

After ventilation, the next most important safety measure is flammable gas detection. This is done by the use of both fixed and portable gas sensing equipment. In simple terms, the fixed equipment will consist of a relatively large control box, serviced by two gas sensing heads (or probes) that are placed at fixed positions in sensitive areas. For example, a gas sensor, which is quite small, may be firmly attached to the exhaust register, in the direction of the flow of released HAP vapors from the gasser, and about 100mm up from floor level. The control box will have either one or two %-LEL dial gauges. If one gauge is used, it will indicate the higher of the two sensor readings. If there are two gauges, they will show the reading of each sensor. These readings are very important since they can give an early detection of problems that can develop into serious situations. They should be checked every 20 to 30 minutes of production time.





**The significance of the %-LEL readings can be outlined as follows:**

0-3% LEL:	Abnormally low during production. Check the instrument.
3-10% LEL:	Typical, during production.
10-20% LEL:	Tolerable, but needs investigation; possible small leakage.
20-40% LEL:	Indicates a serious HAP leakage Emergency ventilation should come on automatically. Low level siren and yellow alarm light should be activated. Immediate investigation for leakage is required.
40% LEL or higher:	Indicates a very dangerous HAP leakage. All but trained emergency workers should evacuate the plant. Production is stopped. Propellant is shut-off to the gasser or gashouse. Propellant lines at the gasser or in the gashouse are drained. High-level siren and blinking red alarm lights are activated. Immediate investigation and correction is required.

There are two types of fixed gas detection instruments available. Both use control boxes, which are not explosion proof and must be located away from hazardous areas. The smaller and cheaper unit operates on a Wheatstone Bridge principle. It is called the "Hot Wire" method. Probes are connected electrically to the control box. A slight disadvantage is that the probes can sometimes be disabled by prolonged contact with silicone mists, and in older models, by chlorinated solvent vapors. The control box can be as small as 300 x 400 x 250mm deep.

The other method uses a spectrophotometric absorption measurement and is called the "Infra-Red" system. Very small copper tubes carry a continuous sampling stream of the gas-air mixture into the control box for analysis. The size of the control boxes varies, but some are 1.8m tall. These instruments are self-checking and very reliable.

All fixed gas detection systems must be installed, checked and calibrated by experts.

The %-LEL gauges should read 0%-LEL when the production line is not operating, even with liquid HAP in the pipes, hoses and filler cylinders. Anything else indicates gas leakage or mis-calibration. Many aerosol plants keep a logbook to record 5% LEL levels. The instruments should be recalibrated periodically using standard gas-air mixtures to fill a small paper bag or balloon that can surround the sensor heads. Gas detectors are more essential when gassers are located inside buildings.

Portable gas detection units are small and some weigh less than a kilogram. They can be easily hand-carried and are used to check for propellant leakage at pipe connections, valves, pumps, filters, molecular sieves and other sites. They are called "Explosimeters" by some people. They signal leakage by a buzzing or clacking sound, which intensifies as the instrument detects higher concentrations of escaped gas. It is not uncommon for aerosol plants to lose from 5 to 10% of their propellant as a result of leakage, plus another 3 to 6% at the gasser. This shows that leakage can be an economic problem in addition to a potential hazard.



Leak detectors such as this one are readily available. They are costly, but are very important for plant safety.

Portable detectors should be used at least once daily to check for leaks. They should be protected from exposure to chlorinated solvent vapors and silicone mists although some models are immune to corrosion by chlorinated solvents. They should be kept clean, given new batteries as needed and calibrated periodically, especially if they are dropped. Since they cost up to US\$1500, they should be stored in a safe place and only used by trained personnel. Regular maintenance and inspection of portable detectors, especially in developing countries where this mode of detection is the most affordable, is critical to plant safety.

The most critical leaks are those in inside locations with little or no air movement. Pumps often leak and pipe flanges, hose connections and gasser heads sometimes leak. Back-welded pipe joints almost never leak and are much preferred over threaded joints and flanges. Leaks can often increase over time. Any significant inside leaks should be corrected without delay. In some aerosol plants, the manager will get a daily "Leakage Report", indicating the leakage status and corrections. This gives him assurance that this important aspect of maintenance is not being neglected.

## Transfer Lines (Pipes and Hoses)

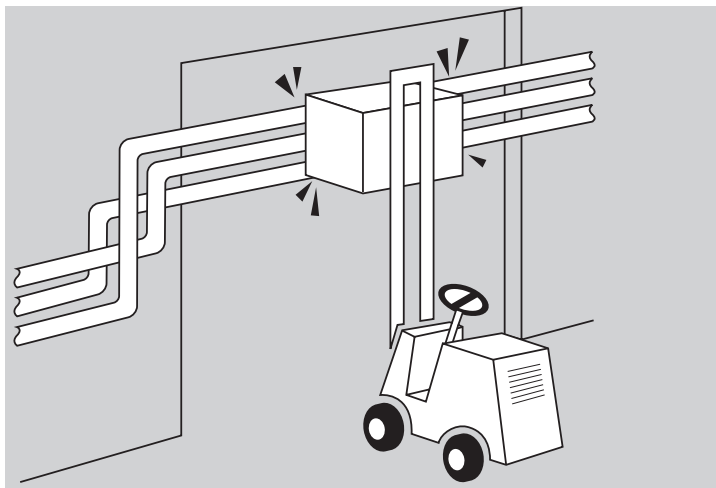
Pipes are required to safely carry liquid propellant from storage vessels to the gasser. For bulk tanks, there will also be a return line. The piping assembly will contain valves, pumps, a molecular sieve unit, a filter and various fittings. Screwed connections will always leak after awhile. If they must be used, the threads must be made using a sharp die, cleaned thoroughly, double-wrapped with Teflon™ sealing tape, and tightened with more force than usual. Flanged connections are more acceptable, but costlier. If they are taken apart, the gasket must be replaced. Back-welded joints are preferred.

Slow and medium speed aerosol lines will almost never require propellant flows greater than about 20 liters per minute. The liquid hydrocarbons also have extremely low viscosities. As a result, relatively small pipelines will be sufficient to carry the propellant to the gasser. If an excessive pressure drop or insufficient flow is noticed at the gasser, the first thing to do is to check the filter that follows the molecular sieve unit; it may be partly plugged.

Every element of the propellant line must be able to withstand a pressure of at least twice the maximum working pressure of the pump, without leaking or rupturing. It is customary to use only heavy-duty (or double-strength) steel pipe, of an optimum diameter. A minimum of 25mm inside diameter is recommended for the liquid line, while the return line to the bulk-tank should be at least 20mm. Sharp turns should be avoided, in favor of rounded turns. Reducer fittings (to accommodate pumps, valves and so forth) should be avoided when possible. Short lengths of flexible hose, down to 20mm inside diameter, may be used as necessary, but they should be rated for service to at least 120 bars, and preferably made conductive, to prevent static charge accumulations.

For propellant service to inside gassers, the pipe length and number of fittings inside the plant must be minimized. Inside hoses should be limited to 2m in length, be free of sharp bends, especially near the connectors, and be inspected regularly for any sign of wear or deterioration. In-plant piping should be frequently supported and be kept well out of the way of lift-trucks. Ideally, it should be painted bright red and placarded with such words as "Propellant – Extremely Flammable".

Severe accidents can occur if propellant pipes can be reached and damaged by lift trucks or other vehicles.



Outside the plant building, propellant pipes must be protected from damage by lift-trucks, tank-trucks or other heavy equipment. To cross-plant roadways, pipes should be at least 7m high, and mounted on steel poles and a steel cross-beam. Underground piping is not recommended. Occasionally piping is passed below roadways using concrete lined trenches, covered by heavy steel gratings. The trench must be drained and periodically cleaned. In tropical countries, this option should be avoided, due to heavy downpours which may lead to flooding and thus heavy corrosion. This option is considerably more costly than overhead crossings.



Trenched propellant pipes are best but somewhat more expensive.



This excellent installation in Thailand shows protection posts, good fencing, and a parallel unloading. Note the height of the "pipe bridge."

Propellant piping installations have occasionally been badly damaged by tank trucks. Ideally, the truck should be able to drive alongside the unloading area, instead of backing up to it. If it must back up to unload, a very heavy, reinforced concrete barrier must be used to stop the truck from backing up too far and striking the pipes. Vertical barriers may damage some trucks. Slanted barriers protect both truck and pipes.

Before unloading propellant into the intake pipes, the tank truck must be electrically grounded, and wooden blocks (chocks) must be placed against the wheels to prevent any movement while unloading. There are at least three instances (all in the USA) where movement occurred. In each one, the hose tore apart and whipped around so violently that the stream of propellant could not be shut off. Now, all USA tank trucks have excess flow valves to prevent any future occurrences. This may not be the case in all countries.

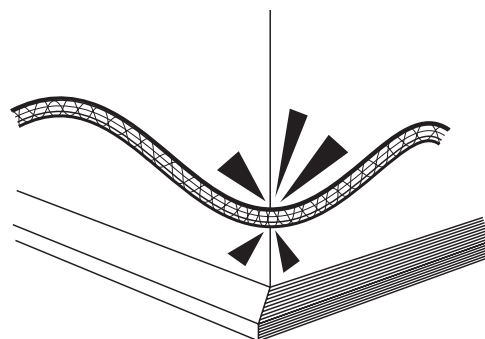
Nearly all aerosol plant fires and explosions are caused by sparks. These sparks must be eliminated as completely as possible. An electrical (static) spark is produced when two objects of different electrical charge come very close or touch each other. One way to eliminate these sparks is to connect all the pieces of equipment in the complete aerosol line, the piping, and the storage tanks. Machines are typically connected together by two copper wires or braids – hanging loosely, so they are able to accommodate minor movements of the machines as they operate. At some point there must be a connection to a grounding (or earthing) pole. This is normally a piece of pointed steel reinforcing rod about 20mm in diameter, driven about 3m into the ground. One plant may have three or four of these grounding rods. They must go down to where the earth is wet and conductive so that resistance will be no more than 10 ohms. In dry conditions, water may be periodically poured into a small hole, surrounding the top of the grounding rod. This will keep all metallic equipment from producing static sparks.

Static discharges can still occur from non-metallic objects. Although rare with hydrocarbons, static charges can accumulate on rubber hoses that do not have stainless steel (or other metal) cores or braided outer coverings. This is a common occurrence in China, where dimethyl ether propellant is quite popular. Static charges can also build up on plastic conveyor belts. For this reason, stainless steel belts should always be used around gassers. Finally, workers who wear clothing fabricated from silk or synthetics will generate a static charge as they move about. This will cause sparks when they touch grounded equipment or walk on conductive concrete or metal floors. A number of small gashouse fires have been started in this way, with gashouse operators and maintenance men getting moderately burned hands. These workers should wear cotton clothing, which does not generate static charges. The wearing of metal-toed shoes gives further insurance against producing static charges in these highly protected areas.

Flexible hoses are usually the weakest point in any propellant transfer system. Hoses that are not made for hydrocarbon service or are made of poor grade materials or are old and worn, can be quite hazardous if they develop major leaks or simply tear open. Excess flow shut-off valves can be installed upstream from flexible hoses but they only work if the leak exceeds the maximum design flow of the piping system. In any event, all the liquid in the hose and all that is downstream (up to any reverse flow shut-off valve) will quickly be discharged. This can be extremely hazardous to inside areas and workers should evacuate immediately if such an event occurs.

Hoses must be properly used and cared for. They should be supported at intervals and kept off of floors. They should be easily visible, from one end to the other. They should not pass through holes in walls or be subjected to excess vibration from machines. Hoses should be kept well away from plant aisles and walkways, should be used only when necessary and should not be longer than 2m. They must be inspected frequently for wear.

They become progressively less reliable as temperatures rise above about 52°C. Welding or other “hot work” should not be done closer than 10m from any propellant pipe or hose. If closer work must be done, it should be approved by the engineering manager, and all nearby pipes, hoses and equipment must first be drained of liquid propellant and flushed with nitrogen. In an African aerosol plant, a small piece of molten steel from a welding operation contacted a nylon-reinforced rubber hose, burning it almost through. When propellant was charged in the hose the next morning, the weakened area burst open. A large amount of HAP was released. Fortunately, no fire or explosion resulted but the building was evacuated until the hose could be safely replaced. Several hours of production time were lost.



Scraping on a corner can cause wear. Rubber hoses must be inspected frequently for any signs of wear.



Small diameter flexible hoses are often used on gassers to supply propellant to the individual gassing heads as they travel up and down. If they touch the central column or other parts of the gasser during their motion, this could create severe wear. Gassers should be inspected for this possibility. Corrections take only a few minutes. Any worn hoses should be replaced using spare hoses kept in inventory in a "Parts Room." The propellant flow in hoses should always be from the male to the female couplings.

## Emergency Equipment and Systems

A number of safety devices are used to protect lives and property. Some will be automatic, as in electro-protective systems, while others are designed for manual operation. Plant requirements will differ, according to the sophistication of their engineers and the degree of management dedication to safety. Larger plants generally need more protective equipment since their operations are more complex and they handle larger quantities of flammable liquids and gasses.

Gassing enclosures (inside and outside) should have one or more manual shut-off switches. They are located next to doorways inside the gasser area. They must be well marked and readily accessible. Key employees, such as gasser operators, must be trained in their location and use. These switches should be immediately actuated in the event of a fire, a ventilation failure, a 40%-LEL (or more) alarm from the flammable gas sensor unit and any pipe, hose or equipment failure that releases flammable gas.

Actuating the emergency shut-off switch will do a number of things: it will shut down the aerosol production line, and it will cause an electrical solenoid valve, normally just outside the gashouse or plant, to close, thus blocking any more propellant from entering these buildings. At the same time, these valves are designed to cause the liquid propellant in the buildings to be evacuated, through a 10 to 12mm inside diameter pipe that extends vertically, to a point well above the roof. The liquid propellant in the pipes, hoses and gasser will fly out of this little pipe and into the air, so that it can safely evaporate and be carried away by the wind. These special solenoid valves are often called "block and bleed" valves, to indicate how they operate.

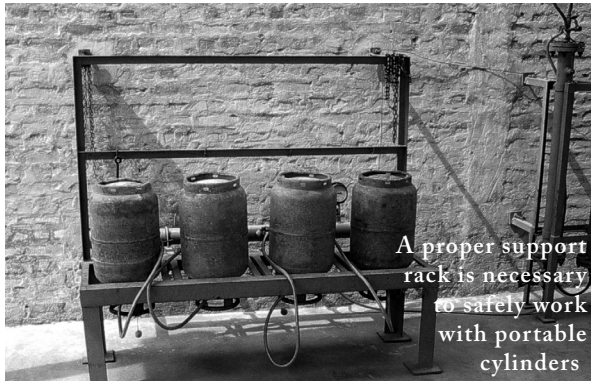
If a fire occurs in a gashouse, it will generally start at the area where the gasser releases the aerosol cans. This is where the HAP gas is most concentrated. It will spread in all directions at about 3.7m per second, to an extent limited only by the fuel supply. Workers standing next to the gasser may be burned and disoriented before they can react. If the fire is relatively small and the operator is not standing too close to the source, he may be able to press a switch that will cause a very heavy, forceful spray of water to be released from sprinkler-heads mounted near the ceiling. This life safety equipment is called a "deluge system." The water will control the fire but more importantly, it will keep workers in the gashouse from being badly burned.

The best "deluge systems" used by most larger fillers are automatically operated. A small box, containing twin flame sensors, is mounted just below the ceiling and adjusted to face the gasser. If a fire is sensed, the electrical system reacts instantly to open a valve and release water into the room. This affords better protection than the manual switch, because it controls the fire before it can reach its full size.

However, regular maintenance and inspection must be carried out, otherwise it is possible that the system will not function properly when needed. Inspections every six months are generally sufficient.

Explosion-proof electrical motors and other equipment is standard for high-hazard areas, such as within 12 to 15m from any gasser, LPG storage tank or molecular sieve. This type of equipment is recommended for the entire aerosol production area since flammable gas vapors could be released from hot water baths, machines that attach buttons or spouts to valves (called "tippers") and so forth. An exception may be made for the gas detection control boxes, since they are normally 1.0 to 1.5m above floor level and the cabinets are tightly closed.

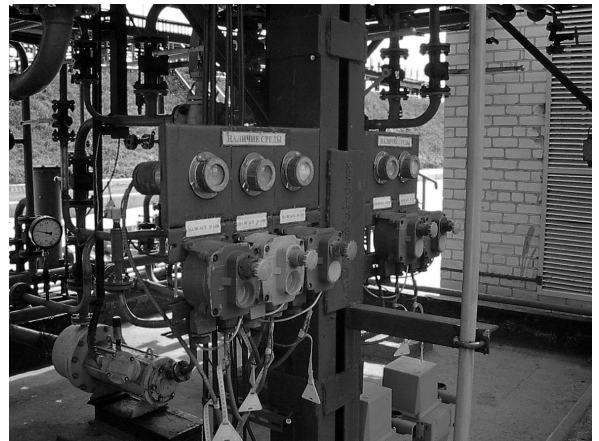
Bulk tanks designed for flammable gas storage should have the same 18 bar working pressure as “propane tanks”; and they will usually have an excess flow valve inside the tank at the liquid outlet pipe. This will shut off the LPG flow if the exit pipe is broken. If the fitting is not provided, it must be installed by the seller or the buyer, sometimes on the exit pipe, just outside the tank itself, but internal excess flow valves offer superior safety.



Where 50kg flammable gas cylinders are used, the pipeline leading from one or more of these inverted tanks should also have an excess flow valve, as close to the cylinders as practical (some of these cylinders may incorporate such valves but that cannot be depended upon). Further, it is essential that they are used strapped or chained to proper cylinder racks, so that they cannot fall and possibly break their connection hoses.

The exit pipeline of an LPG bulk tank will normally carry the excess flow valve, then a regular shut-off valve, and then lead to a low pressure pump. The pump will normally add about 7 to 10 bars to the pressure of the propellant. This prevents gas pockets from forming in the pipeline and helps to force the liquid LPG through the line, against the back-pressure of the return line to the bulk tank. It is vital that the pump, if it is electric, be completely explosion proof.

It is important to station the pump at least 2m away from the “footprint” of the bulk tank and not under any sunroofs. This lesson was learned when the packing gland (journal) of such a pump slowly developed a propellant leak that washed away most of the lubricant. This caused friction and overheating. The leakage rate increased. When the heating became intense, a small flame developed, which caused ignition of the escaping gas. By the time the problem was discovered, a flaming plume of gas, about 25 or 30m high had formed. The pump was below one end of the tank so that the flames contacted a large area of the tank. It was extremely difficult to close the shut-off valve, which was also very hot. Had this not been possible, the tank might have been heated beyond the capacity of the two pressure relief valves, causing it to explode. Bulk tank explosions are extremely rare, but they do occur. Fire balls as large as 200m in diameter will be produced, and quite often, large pieces of the tank will fly through the air for distances of more than 1km.



Excess flow valves (arrow) should always be installed on the outlet of LPG storage tanks.

In warm climates, it is useful to paint bulk tanks and propellant lines with white enamel. This prevents overheating from the sun. As propellant temperature rises, the liquid density will decrease, often requiring changes in the volumetric setting of the gasser. In some cases, tanks are protected from overheating by the use of water sprinklers or sunroofs. Tanks that are relatively empty heat up faster and to higher temperatures than those that are relatively full.

The rapid expansion of LPG liquid with increasing temperature affects plant design and operations in several ways. Bulk tanks, in moderately warm areas of the world, must not be filled to over 85 volume-% of their capacity, as measured by “squirt” or dial gauges on the tank. In hot areas, including most deserts, where temperatures can get to 50°C, bulk tanks should not be filled to over about 80 volume-%, unless the LPG in the tank truck is also relatively warm.

When the steel propellant pipeline is heated by the sun, the metal will expand. To avoid strains, bending and possible rupture, one or more "U" bends of appropriate size should be included in their construction. Finally, the liquid propellant should never be enclosed between two shut off valves. In such a circumstance, if the pipeline is heated, the liquid will expand, creating pressures sufficient to break one of the valves. If a hose forms part of the liquid filled line, it may rupture at one of the connectors before the valve breaks.

Lift trucks, usually powered by motors that use propane as a fuel, are not explosion-proof and must be used with caution. For example, there is no advantage of having explosion-proof electrical equipment in the production area, if mechanized lift trucks can come into that area.

As a minimum, explosion-proof electrical systems must be used near the concentrate filler, inside or outside gassers, propellant pumps, and the hot water bath. The propellant storage area must be explosion-proofed. If an inside or outside gashouse is constructed, all electrical equipment inside the gashouse must be explosion-proof. Vehicular traffic, including tank trucks, must be routed so that they do not approach closer than about 8m from bulk tanks or outside gashouses. Steel girder or reinforced concrete barriers should be properly placed to prevent tankers from damaging piping or from ramming the storage tanks themselves.

Electrical interlocks must be designed to fail-safe specifications, in the event of a power outage.



These enclosed explosion proof lights are from a gassing room in Jordan.

## Construction Aspects

All gassing rooms or areas must be of non-flammable construction. Flammable solvents, wood furnishings and apparel must be kept out of gashouses and preferably away from production lines. All combustible materials: wood pallets, solvents, cardboard boxes, and so forth, should be kept well away from hydrocarbon storage areas, pumping stations and gasser areas. Concrete pads should be provided for all pumps, cylinder racks, molecular sieve assemblies and similar outside equipment.

If a large size gashouse is constructed, ideally it should have two exit doors. One is for workers and the other would be a double door for emergency use and for the transfer of a large gasser, for repairs or replacement. The smaller gashouses, used mainly inside plants, usually have only one door. All these doors are made of steel and must be kept closed when the gasser is running. Ideally, the inside of the doors should have a long, horizontal "panic bar" about halfway up. They are made of metal and simply pushing at them will open the door. They provide an immediate way of leaving the gashouse, in case of an emergency.

Some gassing equipment is so reliable that the gashouse can be left unattended. This is ideal, for safety reasons. These small gashouses only contain the gasser and the conveyors that carry cans in and out through holes in the wall facing the plant. At least four aerosol equipment suppliers make gassers and ventilated gassing rooms that are designed for unattended operation. Optionally, one or two television cameras can be mounted in corners, near the ceiling of these enclosures, and aimed at the gasser. They are connected to one or two television screens in the main plant. The gasser can then be visually monitored to make sure everything is operating correctly.

The larger, outside gashouses may also contain a weight-checking machine, and sometimes a button applicator machine, called a "tipper". It is not recommended to have a "tipper" in the gas house, as it requires regular replenishment of actuators. No other machines should be installed in these enclosures, including propellant pumps and vacuum pumps. A small metal worktable may be in the gashouse and often a small supply of tools, gaskets and other spare parts. A machine set-up checklist and maintenance log book can be kept there for quick reference. Flammable solvents, paper trash, boxes and so forth should not be kept in gashouses.



Any worker who is authorized to operate a gasser or go into a gashouse should receive special safety training. No flames, sparks or hot surfaces are permitted in these areas. This includes cigarettes, cameras, cell phones and regular telephones, hot plates for cooking, welding torches, transistor radios, open electric switches, portable refrigerators and so forth. Some fillers will not permit employees to carry matches or cigarette lighters into gashouses simply because they might try to light a cigarette without thinking of what they are doing. In fact, no lighters or matches should be allowed in the filling plant at all, just as in petroleum refineries. Lighters and matches should be kept only in designated smoking areas.

Workers who have consumed alcoholic beverages, or who use drugs, cannot be relied upon, and should never enter gashouses.

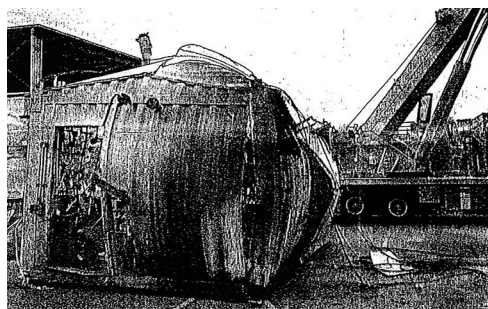
In "atmospheric crimping" there is no attempt to remove air from the headspace of the aerosol can during production. There is another option called "vacuum crimping", where about 60 to 75% of the air is sucked out of the can before the valve is crimped into place. The advantages of vacuum crimping are greatly exaggerated. It can be hazardous, if it is used with volatile, flammable solvents, such as pentanes or hexanes. These liquids will rapidly evaporate or even boil in the can as the vacuum is applied, and the vapors will soon fill the tank of the vacuum pump unit and be emitted from the exhaust pipe. If the vacuum pump is located in an enclosed room or where there is very little air movement, these heavy vapors rapidly sink to the floor and spread. Only about 1.0 to 1.3 volume-% in the air will produce a potentially flammable mixture. During the 1970s, a major USA aerosol plant burned down from hydrocarbon fumes pouring out of a large vacuum pump exhaust pipe. If a vacuum crimper must be used, the vacuum pump should be located in a protected but open outside area.

Some gashouses are constructed of heavy, reinforced concrete walls and have a strong metal roof supported by steel beams. These roofs can be used very conveniently to support fan motors that are used to ventilate the enclosure. The basic structure is built to resist 300 km/hour windstorms, or wall pressures of up to 500 kg/m<sup>2</sup>. If a significant fire occurs inside a gashouse, the pressure, mainly due to the heating effect, can easily exceed the designed pressure resistance of even those strong structures and for this reason, a "blow-out wall section" must be provided. This area may look like large window opening, closed with light sheet metal. It must open in a direction that does not endanger workers or other buildings it case it blows open.

The blow out wall section should be at least one square meter in area for every 30 cubic meters of space inside the gassing room. For example, if the gassing room is 3 x 3 x 3m in interior size (27 m<sup>3</sup>), then the "blow out" area must be 0.9 square meter in area, such as 900mm high and 1.000mm wide. The light metal covering is secured with little pins of soft metal, like lead, that will shear off and let the lightweight metal or plastic panel swing open at an inside pressure of 100kg/m or less. These panels prevent pressure-induced injuries to anyone in the room and prevent the gashouse from blowing apart.

All metal gashouses are fabricated by several equipment suppliers. They come complete with ventilation systems, gas detection devices, water deluge piping and a gasser. If a hydrocarbon fire occurs in these structures, they will be greatly distorted and pieces may blow apart to let out the high pressure. A few years ago, a 3 x 3 x 3m all metal gashouse in the USA had a flash fire. The building had been in the shape of a cube, but afterward it had the shape of an orange.

The "orange shaped" destroyed gassing room.



A steel door blew off and flew about 3m through the air and struck a worker in the chest, killing him instantly. The production line could not operate for almost three months while a new gashouse was installed, fitted with a new gasser and safety equipment and thoroughly tested. The exact cause of the explosion was never determined.

Outside gashouses should be positioned at least 2m from the main plant building, 10m from LPG bulk tanks, and 6m from gas cylinders or molecular sieve stations. Flammable materials, such as wood pallets or boxes of defective aerosol cans, should not be stored near gashouses. Roadways, designed for tank trucks, cars, lift trucks, motorized bicycles and so forth, should not be within 10m of the gashouse. These general considerations also apply to inside gashouses.

#### Additional Accident Examples Part # 1:

The chances of a catastrophic leak from a bulk tank are extremely remote, but such accidents have happened on at least three occasions. In one case, a tank truck was pumping a relatively high pressure LPG blend when the bulk tank became liquid filled. The two pressure relief valves on top of the bulk tank were not sufficient to relieve the combined pressure of the propellant plus the pumping pressure. The tank wall apparently stretched slightly and then tore apart. About 42,000 liters, (42m<sup>3</sup>) of hydrocarbon gas and boiling liquid spilled out, as the two parts of the ruined tank flew for long distances before landing in open fields. The gas caught fire from some unknown source, producing a fireball about 150m in diameter. The direct and radiation heat burned down the aerosol plant and three nearby houses. Some people walking about 200m from the huge fireball were knocked down by the shock wave, and they were badly "sunburned" by the ultra-violet radiation from the fire.

In another case, a 125,000 liter (125m<sup>3</sup>) very large tank car of propane was struck by a large tank car of chlorine. The propane tank was severely cracked. The entire contents escaped in less than one minute, causing the ruined tank car to overturn. The gas ignited and a huge fireball was created. Many people were killed and almost 100 buildings were burned down. This happened in the town of Salem, Illinois, USA. Events like this show that tank trucks must be prevented from hitting bulk tanks as they move into position for unloading.



A huge tank car explosion and fire.

## Safe Operation of Warm Water Baths

The warm water bath normally consists of a long tank of water, heated by the addition of hot water from a steam or electric heat exchanger. One to four lanes of aerosols will enter at one end where the conveyor belt tilts downward, so that they become totally immersed. As they travel slowly through the water, they become quite warm. Near the far end, a trained operator looks for gas bubbles that indicate leakers and for any cans that deform or possibly burst. The cans are then tilted upward and out of the warm water. They are blown dry, using streams of compressed air. Any remaining water will evaporate in a few minutes or less.

The objective of the warm water bath is to heat the cans until they develop the same pressure as they would have if held at 50°C for 30 minutes or more. To do this, the water in the bath may have to be raised to 55°C or even 58°C. It should never be raised above about 62°C, or some perfectly acceptable cans might deform, or even rupture. Aerosol



Plexiglas covers protect workers in case a can ruptures.

cans should not be filled to more than about 90% of their net volume (at 20°C), or the liquid might expand to totally fill the can during warm water bathing. If this happens, any further heating will make the liquid distort the can. In deciding the maximum safe fill per can, engineers must consider the filling and gassing tolerances. For example, an aerosol designed to have an average fill of 90 volume-% of the can net capacity, might actually range from 88 to 92 volume-%.

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Tinplate cans are held down on the hot water bath conveyor belts by magnets, placed just below the belts. Aluminum cans are not magnetic, so the bottom part must be fitted with a "puck". This is a small plastic cup that fits closely onto the can. Each "puck" has a large steel washer around a water drainage hole about 10mm in diameter. The "puck" allows the aluminum cans to be magnetically held down in the warm water bath. If the "puck" fits too loosely in the bath, the can may float up to the surface of the water and just lay there. Such cans are called "floaters". If they are near the incoming hot water, they may become overheated and dangerous. Operators should remove them as soon as they are seen, preferably with metal tongs (grippers).

Most fillers add sodium nitrite ( $\text{NaNO}_2$ ) to their warm water baths to avoid the possibility of rusting tinplate cans or tinplate valve cups. This can be conveniently added as a 10 liter container of a 40% solution of sodium nitrite in water. The minimum concentration is 0.04% in the bath. If a water-leveling overflow pipe is used to also get rid of any contamination on the water surface, the concentration of the sodium nitrite will very slowly decrease. It must be periodically replenished. The concentration can be readily checked by its ability to decolorize a standard solution of potassium permanganate ( $\text{K}_2\text{MnO}_4$ ).

Any leaking or distorted aerosols are usually collected in a metal 40 liter open top drum, near the end of the warm water bath. Unless the drum is fitted with a small pipe that connects to an exhaust system, it should be emptied outside the building as soon as 5 or 10 leakers are collected. Every day the leakers and any distorted cans should be carried to a safe outside location and punctured with some pointed tool. Perforating defective cans is one of the most dangerous operations at any aerosol filling plant. Great care must be taken. Once empty and drained, defective cans may be treated as ordinary trash, but stored in grounded drums or containers. In some countries, drained insecticide or paint cans may still be considered as hazardous waste.

At rare intervals, defective crimping or gassing operations will cause numerous cans to leak. This will often be seen first in the warm water bath. Any large release of HAP gas is quite hazardous, unless the air over the tank is reliably exhausted to an outside location. The HAP gases are up to twice as heavy as air, so the suction system must be as low, above the tank, as practical. For example, exhaust vents 1m over the water will collect less than 1% of the released HAP gases. The best exhaust systems consist of aluminum or stainless steel hoods that extend over the water. A central exhaust duct draws fresh air in from both open ends of the hood. The hood also has windows of Plexiglas™ or some other tough plastic, for operator visibility.

It is important to make sure the warm water bath does not overheat due to some mechanical failure. Causes of overheating include thermostat failure, broken conveyor line, a continuously leaking steam valve, or electrical outage. There have been at least four occasions where many hundreds of aerosol became overheated and burst, destroying the water bath and releasing large amounts of flammable gas. In one instance a temporary fire resulted. If a water bath problem occurs, the operator should immediately shut off the hot water supply. At least two reliable thermometers should be placed in the water bath and cross-checked to be sure the water is within the specified temperature range.

## Other Safety Factors:

It is important to emphasize the need to establish and practice Safe Systems of Work through proven "Permit to Work Systems," including "Hot Work Permits," for all stages of operations, i.e. installation, commissioning, operation & maintenance. It is frightening the number of times one observes welding or soldering taking place near gas lines or tanks.

Emphasis should be made on using anti-static tools by employees during all phases of operation, and in particular during maintenance operation, especially with third party contractors' staff. Workers should dress in cotton clothing and use rubber soled shoes without nails.

All electrical and electronic tools and devices brought into the plant or used within, must be certified as intrinsically safe for use in flammable and explosive environment. This includes devices such as personal pagers, mobile phone handsets, radios and others. This must apply to all third party contractors and visitors.

Proper control of visitors to avoid unauthorized entry into the plant is vital. There must be a strict enforcement of NO Smoking Policy in the plant, preferably with cigarettes and lighters left at the entry gate, or through the use of clearly marked "smoking permitted" areas.

Plant placards are important, such as Warning Signs, Caution Signs, and Advisory Signs, to guide all people working in the plant regarding any precaution needed associated with their work. As noted elsewhere, a clearly marked evacuation route is necessary for each area of the factory. No activity that is potentially hazardous should take place against the back wall of a factory, or in any other place that does not allow a clear evacuation route.

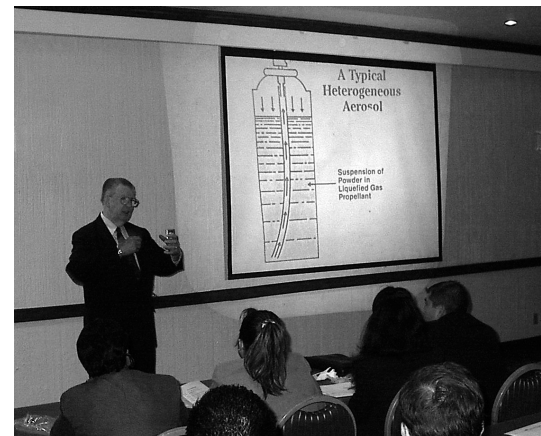
## TRAINING ENHANCES SAFETY

### Training of Employees

One or two engineers should become familiar with this manual, and perhaps other books on safety. They can be called Safety Managers and made responsible for the training of other workers. People working directly with the hydrocarbon propellants should be given extra training. The potential hazard of hydrocarbon gases must be fully appreciated and respected. No one should ever take chances with flammable gases.

People should understand the "Fire Triangle" that gaseous fuel, plus air, plus an ignition source, will produce a dangerous fireball and perhaps an explosion. The ways to reduce hazard, such as reducing the gas concentration below the Lower Explosive Limit (LEL) by ventilation, should be carefully explained.

The significance of small, continuous leakages is often overlooked. If a fire did not happen yesterday, it could still ignite and burn people today. A leak of 10 grams of butanes, in a non-ventilated area, could produce up to 200 liters of potentially flammable gas/air mixture. If a person walked through it and caused a static spark, it could produce about 320 liters of flame volume for a brief period. That person could possibly die. If he or she panicked and took a deep breath of the flames, that would sear the lungs and be 100% lethal.



**Training should be in small groups and carried out continuously. This manual is designed to be used for this purpose.**



### Additional Accident Examples, Part # 2:

In one factory, about 500 to 1000ml. of butane was spilled onto the plant floor. It boiled into heavy vapor, which spread invisibly across the floor, finally contacting a small electric relay switch, about 30m away. It ignited, severely burning the legs of two people and doing minor damage to a pallet of aerosol spray bug killer. The aerosols were prevented from exploding by the plant sprinkler system, which quickly soaked the cardboard boxes and put out the "cardboard fire".

To indicate the potential flammability hazard of one pallet-load of aerosols, on 23 June 2003 in Nagoya, Japan, a small truck crashed into a station wagon carrying 800 aerosol paint products – they ignited. One man was killed by the large fire. The flames rose 12m into the air and 18 fire trucks took 70 minutes to put out the fire completely. Both vehicles were totally ruined. This same event could occur in a warehouse if a lift truck crashed into a pallet load of these aerosols, with some bursting and the vapors igniting. In some cases the cans will deform from the heat and pressure and turn into rockets, capable of starting fires in other parts of the warehouse. Very heavy-duty sprinkler systems are required for aerosol warehouses in some countries. Dedicated areas, maximum stacking heights, limited amounts of aerosols and other restrictions may also apply. Once well started, aerosol warehouses always burn down completely.

One plant in Mexico suffered a fireball when leaking LPG was ignited, apparently by a short circuit. Several workers were burned, two seriously, and only the fact that the plant had a very large open area between the roof and the plant doors avoided this fireball becoming an explosion and killing dozens of people. Workers were able to extinguish several pallets where cardboard cartons were burning with fire extinguishers. Damage was minimal.

In 2003 in Mexico a 20,000 + sq. foot warehouse (2,000 m<sup>2</sup>) burned to the ground. The cause of the fire was never discovered. Initially the fire was contained somewhat with fire extinguishers, while fire hoses were run out. It was discovered that the water pump for the fire protection system was improperly connected, and plant water could not be used. Before the fire department arrived, aerosols began to explode, which required that everyone abandon the area. The warehouse burned to the ground, at a cost of at least US\$ 2,000,000. Had water been available to cool the pallets, this warehouse would probably have been saved.

A small upstairs plant in Mexico burned to the ground and killed one person. The cause of fire is unknown, but apparently it started between this unfortunate worker and the staircase, and he could not escape. Lack of a proper escape route was a contributing factor in the death of seven people in an aerosol fire in India recently. The main initial fuel for the fire may have been LPG, but more likely it was the flammable solvent hexane. The factory was destroyed.

### If a serious leakage of hydrocarbon propellant occurs, it can:

#### ➤ Kill people

- in minutes, if totally burned or flames are inhaled
- in days, with over 70% of the skin area burned
- in up to three months, if 55-60% of the skin is burned off
- hospitalization; very painful; followed by pneumonia, as a rule

#### ➤ Give people terrible burns

- "hair aflame" – produces permanent hair loss
- unsightly burn scars, especially on darker-skinned people
- stiffness and pain, especially when flexing burned areas
- lung damage – necessity to breathe faster (for life)
- partial or total loss of vision
- various illnesses, due to over-taxing the immune system

➤ **Burn down buildings and other property**

- burn down part or, generally, all the aerosol filling plant
- explode gas cylinders, or even bulk tanks, close to the plant
- burn nearby houses and trees
- spraying water can produce dangerous pyrolysis chemicals that are soaked into the ground
- long-term loss of jobs for all company employees
- cause huge increases in insurance, if the plant is rebuilt

Never allow hydrocarbon gases or liquids to flow into floor drains or sumps. They can form gas-air mixtures that can pass through drainpipes for long distances, sometimes being ignited and burning back to the source. HAP flames travel at about 4m per second. No aerosol filling or storage should be below ground, as in a basement room.

### Accident Examples, Part # 3:

The ignition of 60g of butane gas caused a 10m long trailer to burn completely in 7 minutes. Similarly, a 500g can of hairspray exploded from excessive heating and caused a beauty shop and adjoining house to burn down completely in less than one hour.

Large leakages, even if very brief, can have disastrous effects. Gashouses have exploded due to hose ruptures (with no excess-flow valves), leaving a valve open, forgetting to install a sealing gasket in a propellant gassing head, and the puncture of five large hairspray cans by a sharply pointed "star-wheel", used for spacing purposes. In one plant, two people were asked to connect a long hose from a bulk tank to a gasser. One left to take an urgent phone call, leaving his end of the line open in the plant. The other person thought the connection was made, so he opened the valve at the bulk tank. The plant floor was quickly flooded with boiling liquid butane and its vapors. The vapors found an ignition source, some 25m away. A giant fireball resulted and most of the plant exploded. The accident cost 5 lives and 17 others were seriously burned. If it had been a work day, over 200 people might have been injured or killed. Plant repairs cost about US\$ 11,000,000 and the people were without jobs for eight months.

Fires from sustained small leakages can be the same as for brief, large leakages. The results are often disastrous! Large fires can sometimes occur in warehouses. In a warehouse containing mostly aerosol paint, a lift truck was removing a pallet load of 15 liter plastic containers of highly flammable paint thinner from a shelf about 5m high. One case of four containers got loose and fell to the concrete floor, smashing at least one container. The operator should have shut off the lift truck engine. Instead, he tried to leave and sparks set the large pool of spilled liquid on fire. The fire spread under pallet loads of nearby aerosols, setting the cartons on fire. Within one minute, the first aerosols overheated and exploded, producing fireballs about 2.2m in diameter. The warehouse burned for 8 days. The loss was US\$ 82,000,000, not considering business interruption losses, loss of customers, loss of jobs, and much higher insurance costs when the building was finally rebuilt.

A very large automobile parts warehouse in southern Germany employed very poor immigrant workers from Greece. They were permitted to cook meals and sleep in the building after work. One evening a kerosene cook-stove was knocked over, spilling about 4 or 5 liters of kerosene, which then ignited. Nearby pallets of aerosol car-care products were then ignited. The intense fire from bursting cans totally destroyed the building and everything in it. Some lives were lost. The fire loss was estimated at about US\$ 115,000,000. This did not count the loss of jobs, rebuilding costs, and so forth.



A solvent fire precipitated this havoc, which killed several workers, but the principal damage was done by exploding aerosol cans.

A horrendous fire in India resulted in the loss of several lives. A small cigar-like smoke (in India called a "beetie") was tossed lit into a drum of hexane. This may have caused the fire, but the major damage was caused by exploding aerosol cans.

Fires that may occur in the open air can also be dangerous. In one example, a 40mm inside diameter propellant pipe, crossing a plant roadway at a height of about 4.5m, was struck by a new tank truck that had an unusually high exhaust pipe. An elbow fitting was cracked, releasing HAP liquid and gas. The truck backed up, and everyone was so busy looking at the badly bent exhaust stack that the propellant leak was not seen. Suddenly, a large fireball was produced, probably from sparks at a lift truck. One engineer was instantly killed, and the truck driver and two other people were badly burned when their clothing caught fire. After the fireball burned out, people saw a 10m long flame coming from the cracked area. It stopped when an up-stream valve was closed. Later, the pipe was found to be threaded "single strength"; when it should have been welded "double-strength".

In a similar incident, a small diameter propellant hose, quite long, was temporarily laid across an aisle, also occasionally used by lift trucks. Eventually it was run over a lift truck carrying 600kg. of aerosols. The hose fractured near a connector, spraying butane inside the building. A fire resulted. The driver and one nearby worker were badly burned. The fire was put out by closing a valve and using two large extinguishers. A Fire Marshall later stated that using the fire extinguishers saved the building from total destruction.

Fires or explosions can occur when HAPs from leaking aerosols can accumulate. In one case, several hundred cans were crimped with a collet that had a broken segment. They leaked furiously in the warm water bath. Two people were very busy, pulling them out and tossing them into a 125 liter steel collection drum. They were too busy to think about the gas being rapidly released in the drum. Soon, the gas spilled invisibly over the top of the drum and spread across the floor. It ignited, probably from an electrical relay switch. A large flame was immediately produced. Three people were burned. Panels, making up the ceiling, were blown out of place and some were partly burned. The local fire authorities took three days to investigate, before allowing production to continue.

In another example, a technically trained customer representative was in the laboratory of a contract filler, testing some aerosols that had just been produced. Afterwards, he punctured 18 cans of a water-based product that contained 34g of isobutane per can. He did this in an explosion-proof exhaust hood. After a minute or so, the evaporation cooled the remaining propellant so that the gas came out of the can more slowly. Thinking that the cans were almost empty of propellant, the man took them out of the hood and threw them into a plastic trash container. He did not notice that this caused the water-based concentrate to warm up the liquid HAP still in each can. The gas almost immediately filled the trash container, then found its way to the pilot light of a gas-operated water heater, about 4m away. A fireball was produced, about the size of a large car, together with a fairly loud whooshing (or windy) sound, and there was an instant increase in air pressure that affected the ears of about 20 people in that laboratory. Fortunately, the laboratory was quite large, and a back door was open. Otherwise, there would have been an explosion and damage to the building. Also, the two young women who worked in the fire area had just left to get some chemicals, or they would probably have been killed.



The training of factory workers should include the basics of fire safety. They should be alert for any problems, such as leaks, smoking, or smelling anything burning, and immediately report these things to their supervisor or the Safety Manager. They should know where fire extinguishers are and how to use them. They should be told that hydrocarbon propellants are like criminals: if they escape from their confinement, they will try to burn or kill people. Workers should not try to be heroes – like trying to stop gas leakages – unless they are authorized to do so after special training. Almost always, they should walk away quickly, by an assigned route, to an outside location (fire drills should be held periodically, to see how fast the plant is vacated). All employees should work in uncluttered areas with easy access to outside doors. When possible, some rooms should have two exit doors, to avoid employees being trapped should a fire occur between them and one of the exit doors.

Supervisors, managers and general managers should all support employee safety training programs. Without their support, little will happen. Ideally, they should provide a small safety booklet for workers to study. They should authorize periodic fire drills, and they should develop a small cadre of engineers, able to understand and cope with hazardous situations.

Hazardous areas should be designated with warning signs, painted lines on floors, and training. They should be dedicated to the purpose intended and protected against arson and vandalism. This can be done in many ways. Most plants will have walls, fencing, gates with locks, "DANGER" or other placards, and possibly a security guard. There will be written procedures, such as the shutting of certain valves, and the draining of propellant from pipelines when not needed. This is especially important for pipes and equipment inside the plant building. Unauthorized persons must be kept out of gashouses and other sensitive areas. People under about 18 years of age should not be allowed in aerosol plants. This is often a local or national regulation. To the extent that is practical, workers should have walkways that keep them out of the path of lift trucks or in-plant lorries. These vehicles should stop completely, before crossing any of the walkways. Placards that advise against smoking, etc. should be posted as needed.

## **Safety of Employees**

Management is ultimately responsible for the safety of their employees. Safety (security) information should be provided to all employees. This will include the extreme dangers posed by HAPs, the hazardous nature of flammable solvents or corrosive chemicals, and how to remain safe, by logical thinking, not doing hazardous things, and so forth. In larger operations, management support of the use of checklists is vital for the safety of the aerosol filling plant. These include the steps to be taken to safely unload a tank truck, to turn on a propellant supply to the gasser, for maintenance work on a molecular sieve and other complex tasks. A supervisor must be on hand to verify the check list procedure, and authorize the initiation of work.

Management should periodically review compounding, storage and production facilities looking for problems and deviations from safety practices. The location of a propellant pump inside a building is a problem, since they always leak propellant to some extent. Management should provide a reasonably clean and well-lit working environment. Certain employees should be issued protective glasses (goggles), such as workers engaged in gassing glass aerosol bottles.

New employees should receive a short period of safety training (more for those handling propellants and gassers), and be given a small, pocket-sized safety booklet. They should be given instructions on what to do in fire drills or if a plant fire should occur. Employees under the influence of alcohol or drugs should be warned and sent home for the day. Workers who deal directly with propellants and gassers must never be influenced by alcohol or drugs since they could make the plant unsafe for everyone else. In many plants, such workers are discharged after either the first or second offense.



# Technical aspects and operation of a molecular sieve hydrocarbon purification system

## Introduction

The butanes and propane, or mixtures of these three compounds are normally called "Liquefied Petroleum Gases" (or "LPG"). The easiest way to convert LPG to "hydrocarbon aerosol propellants" (or "HAPs") is to use molecular sieve adsorption. This works with only some feedstock, where low unsaturated hydrocarbons are present, but it always results in drastically reducing the characteristic odor of "gas."

Mol-siv (a common abbreviation of "molecular sieve") purification is both simple and economical. The gas to be purified is pumped through a column as a liquid, from bottom to top. The column is filled with 1/8" (about 3 mm) diameter pellets or spheres of molecular sieve materials, the most useful of which is sodium aluminum silicate - molecular sieve type 13X  $[\text{Na}_{86} [(\text{AlO}_2)_{86} (\text{SiO}_2)_{106}] \cdot X \text{H}_2\text{O}]$ .

Due to van der Waals' forces, materials are adsorbed on the pores of the sieve material selectively. Water is adsorbed the strongest, adsorption of sulfur (mercaptans and others) is also quite strong, unsaturates less, and saturated hydrocarbons the least of all. More strongly adsorbed materials will displace other ones in the column, i.e. water molecules will displace sulfur molecules.

## Description of Molecular Sieve Columns

In their simplest form, molecular sieve columns (or towers) consist of: an enclosed round column with top, bottom (normally flanged) and walls sufficiently strong to resist the pressure of the gas and the pumping pressure. As a minimum, either top or bottom must be removable, to permit changing the molecular sieve pellets when necessary.

Actual adsorption depends upon mainly upon contact time. A tall thin tower assures more contact time than a short squat tower. A good relation of usable height to diameter is 15:1 for very small diameter columns to 8:1 on larger diameters. Screens of glass wool or other material must always be used on top and on the and bottom of molecular sieve columns to avoid the pellets falling to the bottom of the column, or following the flow through the top valve. The space occupied by the screens and/or glass wool must be added to the heights used in this discussion.

Each column should have a pressure release valve calibrated at 80% of the rated pressure resistance of the tower. This is very important - these towers are designed to work 100% full, and there is no problem when the lines are open, but should the tower be closed without draining when it is cool, and then allowed to heat up, especially in areas where is large temperature variation eg. Middle East in the summer, the gas will expand and surely rupture the tower if a properly working pressure relief valve is not present.

Expanding liquids exert liquistatic pressure, which rises extremely rapidly with changes of temperature. The possibility that the valve will open must therefore be taken into account in the site placement of the column.

Each column should have quick activation valves - ball valves, for example, on the top and bottom. Each tower should have a pressure gauge, the pressure relief valve mentioned above, and a purge valve at the top exit to allow taking samples of the gas.

Care must be taken when loading the pellets. They are highly hygroscopic (they adsorb water). If the drum they come in or the tower itself are left open for a few hours on a humid or rainy day, the sieve pellets may rapidly adsorb their capacity of water from the humidity in the air. Once saturated with H<sub>2</sub>O, the pellets are useless. They will not adsorb any other material. It is advisable to change mol-sivs during hot, dry, sunny days instead of cloudy, humid days. Never attempt changing mol-sivs during rainy days.

The flow should be «liquid phase» or bottom to top. This is one of the most common errors encountered in developing countries. It appears to come from improper reading of supplier literature. Many of the large absorption towers used initially were for drying of natural gas. This is «gas phase absorption» and is properly done top to bottom. Both experience and careful checking of the literature show that liquid phase absorption - as needed for aerosol propellants - is always done bottom to top. Another serious problem encountered in developing countries is that some companies try to operate their molecular sieves horizontally. It does not work well.

Variations involve using molecular sieve 4A first, or using silica or alumina gel first for drying. This complicates the process, however, and normally produces little savings over correct management of a series of mol-siv columns. There is no savings at all where the towers are to be regenerated. Another variation involves using activated carbon, widely used for deodorization of other substances. There is, however, no proof that this improves the results over just using 13X molecular sieve material alone.

## Sizes - Length and Diameter – and Flow Considerations

Actual adsorption depends mainly upon contact time. Some movement is also necessary - most pores are already filled by propane or butane molecules, and any contaminant molecule must strike properly to displace these and be adsorbed.

A tall thin tower assures more contact time than a short squat tower. A good relation of height to diameter is 15:1 in very small diameters (i.e., a 102 mm (4») diameter pipe could be made 152 cm. (60») long); 12:1 in medium diameters (6» to 12» [153 - 306 mm.] diameters); and 8:1 on larger diameters (18» [459 mm.]) or more for example.

Companies that purify LPG and sell it as HAPs or "odorless" almost always purify on a batch basis. They purify from LPG tank to LPG tank, "dirty" to "clean." But most aerosol fillers purify "in-line," that is they pass the dirty gas from its recipient through the column or columns, and then directly to the production line where it is gassed into cans.

A rule of thumb calculation of contact time can be made by taking half the volume of the column - the other half is filled by the pellets - and calculating the weight of LPG contained. This is divided by the maximum rate of LPG usage in ten minutes - the minimum contact time, to give the minimum column height. For example, a 4» diameter column one meter high will contain a volume of 8,171 cm.<sup>2</sup>(3) Taking 50% of this and multiplying by 0.530 (a typical LPG density) will give 2.17 kg. of LPG. If the fastest filling rate is 10 cans per minute (cpm) of 20 grams LPG each, the calculation  $2.17 / (.020 \times 10) = 10.8$  minutes of contact time, which is sufficient with only slightly contaminated material.

If, however, the fastest filling that is done is 18 cpm of 150 grams LPG each, the calculation would be  $2.17 / (.150 \times 18) = 0.8$  minutes - about 48 seconds - and incomplete adsorption will occur.

Another factor is changeover time. Molecular sieve 13X can, in theory, adsorb slightly more than 30% of its weight in total contaminants. In practice, the flow will tend to channel through the column somewhat, and unclean gas will begin to pass through this channel long before the 30% level is reached. This is called the column «breakthrough» point, where unclean gas has begun to pass through the column. For this reason, horizontal columns are not efficient - the pellets tend to settle and channeling is pronounced along the top of horizontal columns. This leads to an early breakthrough, and if pellets are discarded when gas with odor begins to pass out of the column, much of the adsorption possibilities of the 13X material will not be used.

In practice even a well designed vertical column will breakthrough at 20 - 24% adsorption levels. It is possible to have breakthrough occur at 15% by weight adsorbed of sulfur and water, or even at 10%. This can happen with horizontal columns, or with a short, fat column (when the ratio of height to diameter is improper), or when the throughput is too fast [there is not enough residence - "contact" - time].

The following table will consider two column sizes at one flow (usage) rate taken at 100 ppm and 300 ppm contamination levels (H<sub>2</sub>O and all sulfur):

#	Description	Column #1 (4» X 60») (10X152 cm.)	Column # 2 (6» X 80») (15X203 cm.)
1	Volume at 100% (liters)	11.94	37.03
2	Volume at 100% (liters) / 2	5.97	18.52
3	Weight of LPG - [2] X 0.530 in kg.	3.16	9.81
4	Approx. weight of 13X pellets in kg.	8.36	25.92
5	Contact time in minutes at 2 kg/minute 100 ppm contaminant level scenario	1.58	4.90
6	Contaminants adsorbed at 20 % in kg.	1.67	5.18
7	LPG breakthrough point in kg.	16,716	51,842
8	Time to breakthrough/minutes at 2.0 kg/minute	8,358	25,921
9	Time to breakthrough/days at 480 minutes/day 300 ppm contaminant level scenario	17.41	54.00
10	Contaminants adsorbed at 10 % in kg.	0.84	2.59
11	LPG breakthrough point in kg.	2,786	8,640
12	Time to breakthrough/minutes at 2.0 kg/minute	1,393	4,320
13	Time to breakthrough/days at 480 minutes/day	2.90	9.00

Thus the size of the column, the amount of gas passing through, and the amount of contaminants present in the gas will all combine to determine the changeover time, when production must be stopped and new molecular sieve pellets must be charged into the column. This is a very serious concern where contaminants are high or where very small diameter (50.8 mm. (2») or less) columns. It is simply not possible to be changing pellets several times a day.





The small mol-siv columns in the back outside the wire mesh are suitable for a small enterprise only.

The second scenario indicates a 10% utilization of mol-siv pellets, i. e., breakthrough occurs when the pellets have adsorbed only 10% by weight of sulfur compounds. This will not happen with proper columns and proper residence time. This 10% by weight saturation point should not happen but often does. The common reasons for poor utilization are:

**Humidity:** Both the mol-siv storage drum and the column should never be left open. Mol-siv pellets rapidly absorb moisture, which lowers their duration in use. When breakthrough occurs almost immediately after the pellets have been changed, that almost always indicates that the pellets were exposed to atmospheric humidity.

**Water:** LPG can contain water in liquid phase. This may be "overflow" after an acid or amine wash at the refinery, or it may be due to theft, employees emptying part of the LPG and replacing it with water. Very little liquid water can ruin – saturate - a column immediately.

**Channeling:** Pushing high flow rates through a small inlet pipe can increase channeling. Putting mol-siv pellets directly on top of the inlet can also increase channeling. Usually about 20 cm. of the column height at the bottom is kept empty to allow the gas to slow down and distribute itself evenly. This dead space is not included in the above calculations. All horizontal mol-siv units will have a high channeling effect, and 10% maximum utilization by weight could be expected.



These three columns are sufficient size for a medium sized aerosol filler.

**High Flow Rates:** In the example given above, item # 5 is inadequate for both columns, although both columns are rather large for this type of use. An early breakthrough would be expected with column # 2, and a very early breakthrough with column #1. 2.0 kg. per minute of LPG needs a bigger column than #2 - or better, two columns in series (see below).

Continuing calculations, if we want 10 minutes residence time at 2 kg. per minute flow rate, we must have a column where 20 kg. fits at one time. If half the column space is used by the pellets, then we need one with a total capacity of 40 kg. or 75 liters (40 / 0.530 density of LPG). That is approximately double Column # 2, so we could use a column twice as high. However, very high columns are inconvenient to work with, and some empty space at both ends is still needed.

Usually it is better to increase column diameter. An 8" (20.32 cm.) column diameter would have to be 231 cm. high to have a total capacity of 75 liters. Here the height to diameter relationship is 11 to 1, which is acceptable. A 10" (25.4 cm.) diameter column would have to be 148 cm. high to have a total capacity of 75 liters, but the height to diameter relationship is 5.8 to 1, which is not very efficient. The 8" diameter column should be selected.

The breakthrough point in no way affects the total capacity to adsorb. If more than one column exists, a column that has reached breakthrough can be left on line and it will eventually adsorb its 20+ percent of contaminants, or even approach 30%. With only one column, however, new pellets must be installed and used as soon as the breakthrough point is reached, regardless of the percentage of utilization.

Five quite large columns are sufficient for a large filler.



## Construction of Mol-Siv Columns

An round column is usually made of 80 or 120 scale (schedule) pipe. A pressure flange is welded at each end. Three or more brackets are welded 20 cm. from the bottom to support a course and a fine screen, to support the pellets and allow for the «dead space» mentioned above. Two or three centimeters of glass wool above the fine screen will help contain the pellets and distribute the flow.

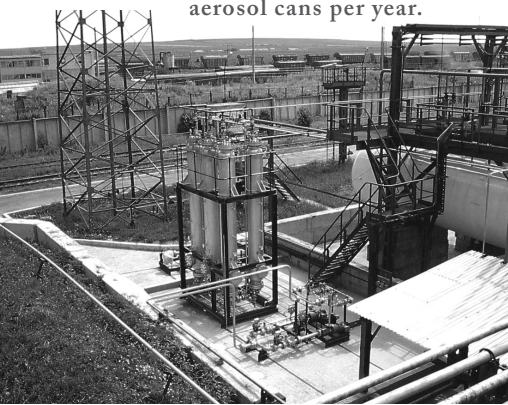
Nibs can be welded to the outside of the column so that it can be supported by an angle iron base. A suggestion is that these nibs be made round, and the base have bearings that permit the whole column to rotate to beyond horizontal to facilitate emptying the used mol-siv pellets.

A gasket and blank thick flange complete the bottom of the column. The blank flange must be thick enough (1" – 2.50 cm. is enough on small columns) to be perforated and for a high pressure (80 scale) nipple to be welded. 3/4" (19 mm.) pipe fittings are adequate for most applications. If a threaded nipple is used, it must be permanently sealed in place with pipe dope (Teflon tape is not acceptable). To this nipple is fitted a high pressure LPG rated ball valve. The inlet hose is connected to this valve. The flanges purchased must withstand 500 psig (about 34 bars) minimum of pressure.

The top installation starts with two screens – fine, which is placed directly on the pellets, and a heavy coarse screen fitting tightly (gripping the inside walls of the column) on top. These detain the pellets. A gasket and blank thick flange complete the top of the column. The blank flange must be thick enough (1" - 2.5 cm. is enough on small columns) to be perforated and for a high pressure (80 scale) nipple to be welded. 3/4" (19 mm.) pipe fittings are adequate for most applications. If a threaded nipple is used, it must be permanently sealed in place with pipe dope (Teflon tape is not acceptable). To this nipple is fitted vertically a high pressure «tee,» and LPG rated

ball valve, and a pressure gauge. The horizontal hole in the tee is fitted with a nipple and LPG rated ball valve, another nipple, and another tee with its vertical hole facing downwards. The horizontal hole in this tee takes the outlet hose. The vertical hole takes a reduction bushing (usually to ¼») and an LPG globe valve for sampling.

Four columns in the Russian Federation for a very large filler, capacity of over 50 million aerosol cans per year.



The top flange itself is perforated to take a pressure release valve calibrated at a minimum of 1.5 times the maximum pumping pressure. This should never be higher than 60% of the rated pressure resistance of the tower. Thus if pumping is done at 200 psig (14 bar), a 300 psig (21 bar) relief valve could be used, if the column had a rated pressure resistance of 500 psig (35 bar).

The bolts used for holding the top and bottom flanges against the column flanges should be the proper ones. Four hole flanges should be avoided if possible - the six or eight hole variety are much more reliable. Usually 3/8» or 1/2» (9.5 mm. to 12,7 mm) hardened steel bolts are adequate. The gasket used on both flange assemblies should be adequate for LPG. Silicone sealant is recommended in addition to the standard gasket to prevent micro leaks, especially on flanges with few bolts.

Best construction has all permanent connections welded. If threaded connections are used, they must be sealed in place with a sealing compound (pipe dope) rather than fixed in place with Teflon™ tape. The sealing must be permanent to avoid their loosening regardless of how many times hoses are connected and disconnected.

## Testing

A certified hydrostatic test should be conducted by an appropriate person. It should be at twice the maximum operating pressure, or 500 psig. The pressure relief valve is removed to allow this test to be done, and the hole is plugged. This is routinely done once every five years. Aerosol gases are not very corrosive, and more frequent testing is not needed.

After that, the column is mounted on its base, connected to hoses, and the entire system is subjected to a Nitrogen pressure test. The column is pressurized to 1.5 times the normal highest pumping pressure, and tested for leakage with foam from soapy water, or with a sensitive portable leak detector. The unit is not commissioned until it passes both tests!

## Economies and Improvement of Efficiency

For aerosol fillers purifying in-line, single column mol-siv units are difficult to run efficiently. Breakthrough always occurs before the mol-siv pellets are completely saturated. With only one column, the pellets must be thrown away immediately and new pellets used.

A three column system is much more efficient. They are used in series as follows:



The quality control or line supervisor checks Column «A» every hour, taking a small sample from the top sampling valve and smelling it. When breakthrough is reached, the sample will have a slight characteristic odor of LPG. At this moment, nothing more is done but placard Column «A» as «used.» Even though breakthrough has occurred, column «A» pellets still have a lot of adsorption capacity remaining.

Thereafter the hourly sample is taken from column "B." When breakthrough is reached on column «B,» production must stop and pellets in column «A» must be replaced. After column «A» is charged with new pellets, the columns are reconnected as follows:

Column «B»  $\Rightarrow$  Column «C»  $\Rightarrow$  Column «A»

After this startup, the first column is always in use beyond breakthrough, but it is kept on stream to use up the residual adsorption capacity that remains. Sampling is always the second column in the series. Now when the second column (Column «C») reaches breakthrough, once again the machine is stopped, and column «B» is changed, and the new re-connection is:

Column «C»  $\Rightarrow$  Column «A»  $\Rightarrow$  Column «B»

The next sequence would be [Column «A» >>> Column «B» >>> Column «C»] repeated.

This ensures that:

- 1) There is always one column – the first one - working beyond breakthrough. This column remains on-line to use up most of the adsorption capacity of the pellets before discarding them.
- 2) The second column has not yet reached breakthrough, but may at any time. When it does, pellets are changed in the first column, and it is re-connected as the final column. The column with the new pellets is always the last column, an important safety feature.
- 3) Thus the third column always starts with new pellets and is far away from breakthrough. No unpurified gas can ever get through to the filling line.

This type of usage of mol-siv columns offers the maximum economies in operation, and also the maximum safety that un-purified gas cannot pass through the system. It is higher in capital investment, but this is rapidly compensated by the operating efficiencies. Adding a fourth or fifth column will squeeze a little more usage out of the pellets, but is not usually cost effective (see exception below). However, additional columns are recommended in countries with high rainfall, since changing of mol-sivs will not be possible during rainy days.

## The Importance of Feedstock

The first fact to remember when dealing with hydrocarbons («HCs») is that they are natural products, not manufactured products. The butanes and propane that we deal with come from the ground. It is possible to know their individual properties very precisely, they are chemical compounds, but when we deal with them as LPG or HAPs, it should be recognized that these materials are not pure but mixtures extracted from the ground, or natural gas streams.



For reference only, this company in Argentina is a supplier of HAPs, they purify LPG and sell HAPs to aerosol fillers. No aerosol filler in the world has columns this big.



Secondly, they cannot just be captured as they come out of the ground. They are always mixed with other materials. Three common mixtures will illustrate this situation:

- From a gas well, mixed with natural gas.
- From crude oil, dissolved in liquid petroleum.
- As a distilled product after «cracking» or «reforming» of heavier HCs.

Separation into individual compounds or groups of compounds is carried out in a petroleum refinery. The fractionation process that physically separates chemical compounds by their boiling points is what establishes the pressure characteristics of the end material, which will be called here “feedstock.” Since this separation is done by fractional distillation, the groupings are called «fractions» or «cuts.»

In theory, as many «cuts» or fractions as there are individual chemical compounds with different boiling points present can be separated. In practice, the purpose of the refinery, and the amount of equipment available, determine the number and character of the different cuts that are produced. If only one fraction is available there is nothing the aerosol filler can do to affect the pressure characteristics of the gas. If two or more fractions exist, the aerosol filler can blend them to obtain different intermediate pressures. Aerosol usage in any given developing country is almost always insufficient to obtain specific «cuts.»

Before the feedstock gets to the aerosol plant, it must be transported inside the refinery, stored there, then transferred to a loading dock, and then transported to the aerosol filling plant. All of these areas have important implications for the aerosol filler.

Aerosol companies would like to obtain the three chemical compounds – n-Butane, Isobutane, and propane – as “pure” cuts, that is 94 – 96% pure. Some refineries have the distillation columns in place to make all three such separations, but this is seldom encountered. So the first problem encountered is what refineries are there, and what columns do they have?

The following are the desired characteristics of a good feedstock:

- Adequate pressure and chemical composition.
- Low in sulfur compounds.
- Low in unsaturated hydrocarbons.
- Low in moisture.

**Pressure/Chemical Composition:** The major components of the chemical composition of a feedstock cannot be changed once it has left the refinery other than by blending it with another material. If a country uses pure propane as LPG, this material will have too high a pressure to be used as a propellant (in most products) without some low-pressure mixture of butanes to blend with it. Serious problems exist (Indonesia, for example) where the only LPG available has a very high pressure.

Some products (paints, solvent based insecticides, some adhesives) need a high-pressure propellant (60-90 psig - 4.1-6.2 bar at 21° C); the majority of aerosol products work best with a low pressure propellant (30-45 psig - 2.1-3.1 bar 21° C). There is no «universal blend,» there isn't with CFCs either. Fortunately there are some uses for pure propane, so many refineries make this cut. Normally, for aerosols, the problem has been finding a low pressure component to blend with the propane.

**Saturates and Unsaturates:** The difference in boiling points between butane (C<sub>4</sub>H<sub>10</sub>) and butene (C<sub>4</sub>H<sub>8</sub>) is slight, and they normally come off in the same cut during fractionation. The butenes with their double bonds are much more reactive than butanes, however, and may contribute to decomposition of perfumes. This is the case with all unsaturated compounds. Also, some of them have a very distinct and disagreeable odor, which is detrimental to an aerosol product. Odor will need to be closely monitored when accepting delivery of HAPs destined to be used in many applications, such as perfumes. That will control unsaturates that have a bad odor.



But it should be remembered always that when double or triple bonded materials react chemically, they may do so quickly, or in a delayed process.

Usually, the source of the feedstock will determine whether unsaturates are present or not. Frequently HC that comes from naturally occurring gas wells is relatively free from unsaturates. Where a refinery with the proper separation towers exists near a gas field, often good feedstock is available. Gas that comes out of crude oil wells frequently has high percentages of unsaturates, and may be unusable as feedstock. Gas from a «cracking plant» is always high in unsaturates.

Mol-siv purification reduces unsaturates only an insignificant amount, so if close odor control is necessary, only those feedstocks are selected that have low unsaturates. Fortunately, refineries tend to source their raw materials continuously from the same place, or by pipeline, Once testing has shown that a given perfume or product can tolerate a given feedstock, then this potential problem is resolved.

Also, many aerosol products – insecticides, paints, and solvent based products – tolerate unsaturates quite well. In some countries unsaturates are not considered a problem. Apparently 80+% of all aerosols in Malaysia are either insecticides or paints, where unsaturates don't seem to be causing significant problems. Even the perfumes filled with locally available gas have been found to be stable.

But where unsaturates are a problem they may be the critical problem, especially with low pressure fractions. It is often necessary to transport feedstock long distances when LPG is available much closer, only because the nearby material is too high in unsaturates to be used.

**Low Sulfur, Low Humidity:** The most common way of purifying HC feedstock for aerosol use is by molecular sieve adsorption. The pellets used are selective in terms of which chemicals they absorb strongly and which they do not. The product that is adsorbed most strongly of all is water. It is therefore very beneficial to have a dry feedstock, as the adsorption power of the material can then be used to remove Sulfur compounds as intended, and not just for drying. Feedstock that is too wet requires pre-drying. Generally, water must be below 100 parts per million (ppm); the lower, the better.

Similarly, the lower the sulfur compound level, the easier it is to clean the feedstock. It is Sulfur (in the form of both H<sub>2</sub>S and mercaptans) that gives LPG its characteristic «odor of gas.» The more of these compounds present, the more pronounced the odor. Experienced LPG people can often give very good estimates of Sulfur content from the odor of the gas long before the results are available from the gas chromatograph.

**The more H<sub>2</sub>O and Sulfur present, the shorter duration of the molecular sieve pellets.**

The saturation level for water in propane is 160 ppm, for iso-butane 84 ppm, and for n.butane 72 ppm at 21 degrees C. So depending upon the product to be filled, the aerosol plant will source feedstock first according to pressure and to how much unsaturates the product can tolerate, and then the material with the least amount of water and sulfur will be selected. Often accurate chemical analysis are unavailable, and these concepts must be defined by practice and experience.

## LPG Stenching

The So far we have identified the bad smell or stench of LPG as coming from Sulfur compounds, and as something that comes from the ground. Sometimes it does. But some gas wells supply raw material that has almost no sulfur compounds at all. Much of the material coming out of the Persian Gulf has very low odor, and some of it would be considered "odorless" as it comes out of the ground. This would make very good feedstock indeed for aerosols!

Unfortunately almost all countries require LPG to be immediately stenching. Mercaptan is added to the material as a safety measure, so that the LPG will “smell of gas.” Correctly stenching LPG will have at least 10 ppm of mercaptans, which is eliminated fairly easily, but due to carelessness, the actual amount is often much higher.

Some countries permit the purchase of odorless or unstenched LPG from a refinery if there is a legal agreement that material so purchased will never be used for fuel. If this is possible it is of course desirable to do so.

The aerosol filler doesn't know – and doesn't care – whether the feedstock received has naturally occurring mercaptans or whether it has been deliberately stenching to comply with handling and transport rules. But it should always be remembered that the amount of sulfur compounds present will determine the duration of the columns between replacements of the pellets.

## Disposing of Used Molecular Sieve Pellets

Used mol-siv pellets stink! They contain many times the same substances that cause the bad odor of LPG. They are also completely saturated with LPG, and as such are a serious flammability hazard. First what not to do:

- Don't discard used mol-siv pellets in the plant garbage bin. Besides the bad odor, the flammability danger is great.
- Don't put them in a drum and seal it. If the ambient temperatures rise later, pressure can build up and rupture the drum.
- Don't pour water on them. Adsorption produces heat, which might cause ignition of the LPG.

What to do? One company empties pellets directly into 20 liter pails of water, little by little, using several different pails of water. Only moderate heat is generated that way. Another spreads them out on a concrete pad and sprays them with water mist until they are fully soaked. In both cases, this occurs in the safe tankfarm area, well ventilated, and with no source of ignition nearby.

Afterwards, the completely wet and therefore inert pellets are loaded into a 200 liter drum with a couple of small pressure relief holes and given to the dealer that handles hazardous, toxic waste for disposal.

## Regeneration of Molecular Sieve Pellets

Virtually all companies that produce HAPs as a business regenerate their 13X pellets. As HAPs supply is their business, they have invested significant amounts of money to establish their capability to regenerate. Such purification plants almost always have large amounts of empty space, and their well-trained staffs work with large volume of odorless LPG continuously. [For that reason, where a qualified supplier of HAPs exists, it is always recommended that the aerosol fillers use them and buy HAPs already purified, rather than engaging in self-purification].

Technical literature indicates that regeneration can be done with a combination of heat and a carrier gas. Sometimes vacuum is mentioned also. In practice, no aerosol filler completely regenerates their pellets. A few heat them up and claim to get some extra use time out of their pellets, but this has not been verified and if it is being done, it would be very dangerous. So this section exists solely to explain how complicated regeneration is, so as to discourage individual experimentation.

Companies that sell HAPs to aerosol fillers regenerate their pellets inside the columns, in the following fashion:

- The columns are insulated to hold heat.
- HAPs suppliers always have storage tanks, they process on a batch basis. Clean HAPs is heated and passed through the column in counter-current, that is, from top to bottom, in vapor phase.

- Initially the HAPs temperature is about 150° C, and this is increased slowly over a period of 2 – 3 hours to 325° C. The flow then remains until a full 12 hours have transpired.
- For safety reasons, the HAPs is only heated indirectly, in a salt bath or other type indirect heater.
- After passing through the column, the LPG is very dirty and contaminated. It must be cooled to liquid phase (or compressed to liquid phase), passed through a liquid separator, and then stored or flared.

For environmental reasons, flaring this very contaminated material is prohibited in many countries. The water removed in the liquid separator is contaminated, and must be disposed of as liquid toxic, hazardous waste.

Since most countries allow a considerable range of mercaptans used for stenching, possibly the best way to dispose of the very dirty LPG that has been used for regeneration is to sell it to an LPG dealer, who will add it into the normal LPG supply tanks little by little, without exceeding the permissible limit.

## Importation

Importing HAPs where not available is an option, but may be difficult and expensive. HAPs can only be transported in pressure vessels. Some typical sizes are given below, in the understanding that local transport regulations may be different from country to country:

Typical Transport Equipment:	Capacity at 90%		
	(gallons)	(liters)	(kilograms)
Road Trailer	10,000	37,850	19,200
Large Rail Tankcar	30,000	113,550	57,600
Ocean Going Isotainer	6,000	22,710	12,260

(An average density of 0.540 kg/liter is used to calculate the «weight capacity.»)

Complicating the problems caused by transport vessels of small size is the need to transport HAPs only in «dedicated» tanks. The tanks cannot be used for any other substance, and must be returned to the supplier when empty. This increases substantially both the operating expenses (the return of the empty vessel or transport equipment) and cost of investment (empty containers must be supplied taking into account the round trip shipping time plus a safety factor, allowance of extra time to cover delays).

Importing avoids the costs of mol-siv columns and solves any problems related to feedstock. But many problems relating to specifications and distribution still exist. Some of these are:

- What gas should be imported, high or low pressure?
- How and in what equipment will the HAPs be delivered?
- How will the pressure be adjusted, and by whom?

Taking these difficulties into account, it may be stated that importation works well if:

- The market is small.
- No source of feedstock is available.
- No «national interests» problem – import controls or licensing - impedes importation.

Under other circumstances, individual enterprises should be better encouraged to use molecular sieve purification.

## Hydrogenation

This is a very sophisticated chemical process which eliminates unsaturates. It is best carried out in a refinery. A few companies worldwide that purify and sell HAPs use this process, but no aerosol fillers do.

## Conclusion to Section # 2

The predominant way of converting butane, propane, or mixtures (LPG) into HAPs is to use molecular sieve adsorption. This is simple and economical. This section gives the basic design and operating parameters for mol-siv columns and explains their construction.

# Modern Aerosol Formulations

## INTRODUCTION

In developing nations most aerosols now use hydrocarbon propellants. Some are still made with CFCs, and China uses dimethyl ether and also carbon dioxide. The purified hydrocarbons (HAPs) offer significant savings. They also allow the production of many water-based products not possible with other propellants except DME, which is often not available in developing countries.

The formulation of good, hydrocarbon-based aerosols can be difficult. There are almost no sources of information, such as books or magazines. On-the-job training can take years. Certain containers and chemicals may not be readily available. The formulator must consider many different aspects:

Stability	The product will not corrode the can or valve. It will not change color, odor or appearance on aging. It will not be degraded by micro-organisms (bacteria, etc.).
Cost	It must be low enough in cost to be competitive.
Regulatory Compliance	
Production	Ability to use present production equipment, if possible.
Safety	Safe to produce. Safe for the consumer, when used as directed.
Utility	Works well. Meets label claims.

The formulations we will show here are some of the best in the world. They are either commercial, in the USA or Europe, or are slightly adjusted, for reasons of confidentiality. Some may have to be changed slightly, to better meet the expectations of local consumers.

## GENERAL PRINCIPLES

Hydrocarbon Aerosol Propellants (HAPs) are poor solvents for water, glycols, resins and other ingredients. Co-solvents, like ethanol, can be used to solublize these chemicals. In some formulas the HAP will remain insoluble. In many water-based cleaners, air fresheners and insecticides, it floats on top as a separate liquid layer. These products cannot be made with CFCs, which are heavier than the water layer.

Aerosols that use HAPs are always more flammable than those with other propellants. The sprays of all anhydrous HAP aerosols can be ignited with a match flame. The sprayed surface can also be ignited, until the HAP and solvents evaporate. The label should warn consumers that these products are "Flammable"

HAP formulas that also contain from about 65 to 95% water are essentially non-flammable. When water is present there is the possibility of corrosion, and corrosion inhibitors must be added. About 0.15% of sodium nitrite ( $\text{NaNO}_2$ ) is often used. Water is hard to break up, so a relatively coarse spray is generally produced, compared to anhydrous formulas. Some water-based concentrates may contain insoluble ingredients, like silicone or perfume oils. They can be dispersed by adding surfactants. The stability of these emulsions must be checked. If there is any slow separation, the feed line from the tank to the filler must be recycled back to the tank at all times. Also, the liquid in the concentrate tank and filler tank must be constantly stirred.



The addition of water will always reduce product costs. Ideally, the water should be purified, at least by reverse osmosis, and preferably by using a mixed bed deionizer unit. Otherwise, variations in the water composition (like chlorine) may be harmful to the aerosol formulation.

In general, HAP formulas will be lower in density – less weight per can – than the old CFC formulas. This is because the hydrocarbons have densities of only about 0.53 gram per milliliter at 20°C. Or about half the density of water. Corrections involve using fill volumes up to about 88% of the net can capacity, labeling in milliliters (mL), or using a somewhat larger can. Some marketers have used the same weight of active ingredients per can, as in the old CFC formulations.

Aerosols containing more than about 5% HAP may be labeled as “Flammable.” If the formula has about 65% water, but more than about 30% HAP, it may be labeled as “FLAMMABLE.” This serves to warn and protect the consumer. A small flame symbol is also used in some cases. Precautionary statements should be included, such as a warning to keep the spray away from flames or sparks. In general, aerosols should be kept out of the reach of children. These precautionary statements usually appear on the back of the can label.

## FORMULATION AND PACKAGING DATA

The following 12 aerosol products have been selected for their diversity and popularity around the world. They are divided into pesticides, cosmetics, household products, and an industrial product.

### Pesticides

The following 12 aerosol products have been selected for their diversity and popularity around the world. They are divided into pesticides, cosmetics, household products, and an industrial product.

#### **Anhydrous (Oil-based) Flying Insect Killer**

Substance	Supplier	% Wt.
Prallethrin (100% Basis)	Sumitomo	0.500
d-Phenothrin (100% Basis)	Sumitomo	0.125
MGK-264 Synergist	Sumitomo	1.000
Fragrance – Optional		0.125
Deodorized Kerosene		58.250
Hydrocarbon Propellant Blend (Pressure: 4.8 bars at 21°C.) [Possibly 38% propane and 62% iso-butane by weight].		40.000
<b>TOTAL</b>		<b>100.000</b>

<b>Can</b>	65 mm diameter, plain interior can is preferred.
<b>Valve</b>	Plain cup, with either a polyethylene sleeve or polypropylene laminate. 0.46 mm stem orifice, buna stem gasket, 0.40 mm mechanical break-up button, or upward spraying full diameter spray dome.
<b>Notes</b>	<ul style="list-style-type: none"> <li>• Quieter spray than water-base formulas, but more costly.</li> <li>• Very flammable</li> <li>• If a 4 m x 4 m room is sprayed for 12 seconds, 100% of flying insects and 90% of crawling insects will be killed.</li> <li>• Cyphenothrin (Sumitomo’s Gokilaht) can be used instead of Prallethrin.</li> </ul>

**Water-based Flying Insect Killer**

Substance	Supplier	% Wt.
d-Allethrin (Neopymamin Forte - 100% Basis)	Sumitomo	0.150
d-Tetramethrin (Neopynamin - 100% Basis)	Sumitomo	0.110
Cyphenothrin (Gokilaht - 100% Basis)	Sumitomo	0.110
Piperonyl Butoxide		0.320
Oleamide DEA (Witcamide 511C)	Witco Chemical	0.180
Sorbitan Monooleate (Arlacel 83, by Uniqema; or Crill 43)	Croda Inc.	0.005
Deodorized Kerosene		8.500
Fragrance – Optional		0.100
De-ionized water		60.207
Octoxynol-9 (Triton X-100)	Rohm & Haas	0.018
Sodium Nitrite		0.150
Sodium Benzoate		0.150
Hydrocarbon Propellant Blend (Pressure = 2.8 bars at 21°C.) Could be 9% Propane and 91% iso-Butane, by weight		30.000
<b>TOTAL</b>		<b>100.000</b>

Can	Tinplate, 65 mm diameter, single lined and side seam striped.
Valve	Tinplate mounting cup, with polypropylene laminate lining. Outside is plain. Use a 0.61 mm stem orifice, buna stem gasket, body with 0.41 mm vapor tap and large tailpiece orifice, preferably for a 1.5 mm capillary dip tube. Use a slotted 0.51 to 0.58 mm actuator, to spray upward, and fitted into a slotted plastic, full diameter spray dome.
Batch Making	Blend the first 8 ingredients in a large mixing tank. This is the oil-phase. Combine the next 4 ingredients in a second large mixing tank. This is the water-phase. With good agitation, add the water-phase to the oil-phase. Maintain slow agitation for the milky concentrate. Fill it using a recycling pipeline that returns to the tank. Ideally, adjust the pH to 7.6 to 8.0 at 25°C.

The **crawling insect killer** is useful against roaches, ants, ticks and other bugs. It is sprayed on the edges of floors and under stoves and cabinets, where these insects hide. Anhydrous formulas are too flammable if they use a hydrocarbon propellant. Many use carbon dioxide. Less costly water-based formulas are available that only use about 4% hydrocarbon propellant, and these are safe to use. This type is now shown:

#### Water-based Crawling Insect Killer

Substance	Supplier	% Wt.
Dursban (Chlorpyrifos)	Shell/Sumitomo	0.500
Xylene	Shell	0.350
EG-5 Castor Oil (Surfactol 318)	NL Chemicals	0.850
Oleamide DEA (Witcamide 511C)	Witco Chemical	0.450
Fragrance – Optional		0.050
De-ionized water		93.600
Sodium Nitrite		0.050
Sodium Benzoate		0.250
Hydrocarbon Propellant Blend (Pressure: 3.5 bars at 21°C.) Could be 18% Propane and 82% Iso-butane, by weight.		3.900
<b>TOTAL</b>		<b>100.000</b>

Can	52 or 65 mm diameter tinplate can, single lined and side seam striped.
Valve	Plain tinplate valve cup, with a polypropylene laminate lining. 0.43 mm stem orifice. Buna gasket. Large liquid orifice valve body – no vapor-tap. Use a button with 0.50 mm diameter mechanical break-up orifice. Standard dip- tube, oriented with curvature toward direction of spray. Spray domes are increasingly used.
BATCH MAKING	Blend the first three ingredients, plus any perfume, in a large mixing tank. Blend the remaining ingredients in another large tank. With good mixing, slowly add the water-phase to the oil-phase. Continue to slowly agitate while filling, and use a recycling piping system for best result. Ideally, adjust the pH to 6.9 to 7.3 at 25°C.
NOTE	Mark the aerosol can with “Shake Before Use”

The final pesticide is the **disinfectant-deodorant spray**. It is designed especially for hard surfaces, such as kitchen countertops, and will kill 99.9% of all bacteria and other micro-organisms within a few minutes. Either carbon dioxide or the hydrocarbons can be used for propellants, but carbon dioxide is often corrosive with water and will require the use of excellent can linings and combinations of inhibitors. Manufacturing is also more difficult. Most marketers prefer to use hydrocarbon propellants.

### Disinfectant-Deodorant Spray

Substance	Supplier	% Wt.
BTC 2125M (50% in water)	Stepan Company	0.300
Atlas G-271 (Soya morpholinium ethosulfate)	Uniqema Inc.	0.100
Morpholine – Low Odor		0.150
Sodium Nitrite		0.200
Fragrance		0.250
De-ionized water		14.000
Ethanol		63.000
Hydrocarbon Propellant Blend (Pressure: 3.5 bars at 21°C.) Could be 18% Propane and 82% Iso-butane, by weight.		22.000
<b>TOTAL</b>		<b>100.000</b>

Can	65 mm diameter, plain inside tinplate cans are referred.
Valve	Tinplate mounting cup, with polypropylene laminate lining. Stem orifice 0.46 to 0.50 mm. Neoprene stem gasket. Actuator is 0.50 mm mechanical break-up, with straight taper. Optionally, this actuator can be slotted, and used with a full-diameter spray-dome.
Compounding	Dissolve the first 4 ingredients in the de-ionized water. Add the ethanol, and then the fragrance.
Notes	The BTC 2125 can be described as: n-Alkyl (60% C14, 32% C12, 5% C16 & 5% C18) dimethyl benzyl ammonium chlorides 0.075% and n-Alkyl (68% C12, 32% C14) dimethyl ethyl-benzyl ammonium chlorides 0.075%. The two ammonium quaternary salts are said to be synergistic. The BTC 2125 can also be used at 0.40%, for still more killing power.
Other	Ammonium quaternary salts are also widely used, such as alkyl (50% C14, 40% C12 & 10% C16) dimethyl benzyl ammonium chloride at 0.12%.

## Cosmetics (personal care)

**Hair spray** preferences regarding particle size, fragrance intensity, hair-holding ability and so forth vary widely. In the USA about 42% water is required to meet air quality regulations. The further use of methylene chloride is banned in some countries. This has caused hair sprays to have larger particles, except in parts of Europe where dimethylether is used as the propellant. The amount of hydrocarbon that can be used in hair sprays is often limited to about 25 to 40% by the type of resin that is selected.

### Hair Sprays

Substance	Supplier	% WT.	
		Regular	Hard to Hold
Amphomer (28-49-10) (97%)	National Starch & Chemical Co.	1.240	1.470
2-Amino- methylpropanol (95% AMP)	Angus Chemical Co.	0.190	0.250
Ethanol 100%		68.470	57.920
Fragrance		0.100	0.360
Hydrocarbon Propellant Blend (Pressure: 3.5 bars at 21°C.) Could be 18% Propane and 82% Iso-butane, by weight.		30.000	40.000
<b>TOTAL</b>		<b>100.00</b>	<b>100.000</b>

Can	Either plain inside tinfoil or lined aluminum.
Valve	Mounting cup of tinplate, with polypropylene laminate lining. 2x0.50 mm stem orifices. Buna stem gasket. Body has a wide open tailpiece and a 0.41 to 0.56 mm vapor-tap. The dip tube is preferably a 1.25 mm inside diameter capillary type. The actuator has a 0.41 mm mechanical break-up (standard taper) orifice. The 0.56 mm vapor-tap is preferred for the "Hard-to-Hold" formula.
Notes	If more hydrocarbon propellant is required, for a "drier" spray, then the use of Versetyl-42 (28-49-42) resin (National Starch & Chemical Company) is suggested. Use the same levels as the Amphomer. Many formulas contain small amounts of animal protein, aloe vera and even vitamin A. They offer minor advantages, but make labels more interesting.



The **hair sheen** is designed to give hair a healthy looking shine. It has very limited holding or styling ability. Hair sheens are very flammable, and leave the hair somewhat more flammable, before the volatile ingredients fully evaporate.

### Hair Sheen

Substance	Supplier	% Wt.
Isopropyl Myristate	Croda Inc.	3.000
Cyclomethicone	Dow Corning Corp.	2.500
Keravis (strengthen conditioner) – optional	Croda Inc.	0.400
Fragrance		0.100
Ethanol		54.000
Hydrocarbon Propellant Blend (Pressure: 3.5 bars at 21°C.) Could be 18% Propane and 82% Iso-butane, by weight.		40.000
<b>TOTAL</b>		<b>100.000</b>

Can	Usually a 65 mm diameter, plain inside tinplate can.
Valve	Mounting cup is plain tinplate, with polypropylene laminate or PE sleeve. Stem orifice is 0.51 mm diameter. Buna gasket. Large liquid orifice valve body, as 2.00 mm. No vapor-tap. 0.41 mm diameter mechanical break-up standard spray actuator. (Alternate: 0.41 mm reverse-taper actuator.)
Notes	Keravis also plasticizes the hair and lubricates the surface to protect the cuticle. The cyclomethicone (silicone) with a five-silicon membered ring is preferred.

The **personal (underarm) deodorant** is extremely popular. The ideal deodorant is called Triclosan, which safely and effectively kills over 99.9% of skin-resident bacteria that are the cause of underarm odors. For most people, spraying once each day is sufficient to control underarm odor. Spray each underarm from 200 to 300 mm for about 2 seconds.

Many people use these sprays to control odors from the feet and other areas. A "body spray" can be formulated, using about one-half the usual level of Triclosan deodorant. Finally, a body cologne can be produced by further reducing or eliminating the Triclosan and increasing the fragrance level.

### Personal Deodorant Spray

Substance	Supplier	% Wt.
Triclosan (Sold as Irgasan DP-3000)	Ciba-Geigy	0.150
Propylene glycol		0.250
Isopropyl Myristate		1.600
Fragrance		0.300
Ethanol		52.700
Hydrocarbon Propellant Blend (Pressure: 3.5 bars at 21°C.) Could be 18% Propane and 82% Iso-butane, by weight.		45.000
<b>TOTAL</b>		<b>100.000</b>

Can	A 52 mm diameter single-lined tinplate or lined aluminum can.
Valve	The mounting cup is plain tinplate, with either a PE-Sleeve or a polypropylene laminate inside. Stem orifice is 0.46 mm. Buna gasket. Body has a large tailpiece orifice (as 2.00 mm) and a 0.40 mm vapor-tap orifice. The actuator is a mechanical break-up (standard orifice) type, with 0.40 mm terminal orifice.
Notes	The vapor-tap reduces delivery rate and produces a warmer spray. As with all anhydrous ethanol batches, they must be protected from adsorbing moisture, which could cause can corrosion. This is done by using covered tanks and minimizing storage time.

**Shaving creams** are of the original pre-foaming type, and now the gel, or post-foaming type. In North America the post-foaming type is 54% of the market. They emit a clear or opaque gel that springs into a heavy foam when touched with the fingertip. These products require special aerosol cans and are difficult to formulate and produce. As a result, we will describe only the original shave creams, which have used hydrocarbon propellants since 1953.

### Shaving Cream

Substance	Supplier	% Wt.
De-ionized Water		74.900
Stearic Acid - Low odor		6.000
Lauric/Myristic Acids - From coconut oil		1.500
Lauryl/Myristyl Diethanolamide (As Schercomid SLM-S)		0.500
Triethanolamine (99%)	Dow Chemical Company	3.900
Cetyl Alcohol		0.500
Glycerin (96 to 99.5%)		5.800
Mineral Oil		2.400
Methyl Paraben (Methyl 4-Hydroxybenzoate – Preservative		0.100
n,Propyl Paraben (n,Propyl 4-Hydroxybenzoate – Preservative)		0.030
Fragrance		0.370
Lanolin Alcohols (Optional)		0.500
Hydrocarbon Propellant Blend (Pressure = 3.5 bars at 21°C.) Could be 18% Propane and 82% Iso-butane, by weight.		3.500
<b>TOTAL</b>		<b>100.000</b>

Can	Lined 52 or 65 mm diameter tinplate or aluminum can.
Valve	Mounting cup is tinplate, with polypropylene laminate lining, for tinplate cans. (Use buna lathe-cut gaskets and lined aluminum cups for aluminum cans). Stem orifice: 0.46 mm. Buna stem gasket. Valve body with typical 1.5 to 2.0 mm (wide open) tailpiece, and no vapor tap. Standard diptube.
Notes	<ul style="list-style-type: none"> <li>• If the Lauric/Myristic Acids ingredient s hard to obtain, it may be replaced with 1.5% additional Stearic Acid. The resulting product will be very slightly harsher on the shaved skin.</li> <li>• This product may also be used when shaving hair from the underarms, legs and other areas.</li> <li>• The foam from all pre-foaming shave creams will become "wetter", or higher in density, when cans are close to emptiness.</li> </ul>

## Households Products

Worldwide, the most popular household aerosol product is the **air freshener**. Many of these formulations are anhydrous, using ethanol, isopropanol, deodorized kerosene or even methanol as the solvent-diluent ingredient. The least costly formulas now use about 68% de-ionized water, together with 30% hydrocarbon propellant. The water-in-oil emulsion sprays more loudly than the anhydrous products, and the average particle size is a little larger. Almost all of these water-based air fresheners are designed to use full-diameter plastic spray domes that allow upward spraying. This helps to deodorize the entire air space in rooms. Typical fill weights are 200 to 300 g. per can.

### **Water-based Air Freshener**

Substance	Supplier	% Wt.
De-ionized Water		68.547
Octoxynol-9 (As Triton X-100)	Rohm & Haas Company – USA	0.018
Sodium Nitrite (Corrosion Inhibitor)		0.105
Sodium Benzoate (Corrosion Inhibitor)		0.105
Glutaraldehyde - 25% in Water	Union Carbide Corporation, now Dow	0.050
Oleamide DEA (As Witcamide 511C)	Witco Chemical Corporation	0.180
Sorbitan Sesquioleate (As Crill 43)	Croda, Inc.	0.005
Fragrance		1.000
Hydrocarbon Propellant Blend (Pressure = 3.5 bars at 21°C.) Could be 18% Propane and 82% Iso-butane, by weight.		29.990
<b>TOTAL</b>		<b>100.000</b>

Can	Usually a 52 mm diameter, lined tinplate can. Lined aluminum cans may also be used.
Valve	<p>The mounting cup is of tinplate, with a polypropylene laminate lining, for tinplate cans. Alternately, use a tinplate mounting cup, epon-phenolic lined, and with a PE-Sleeve, for tinplate cans. For aluminum cans, use lined aluminum mounting cups with buna lathe-cut gaskets. The stem orifice can be from 0.51 to 0.64 mm. The valve body is designed fit a capillary dip-tube, and has a 0.38 to 0.41 mm vapor-tap orifice. The stem gasket may be either buna or neoprene. The capillary dip tube has a 1.27 mm inside diameter. Full diameter spray-domes are almost always used. A slotted, vertical spraying actuator is fitted onto the valve stem, and into the spray -dome. The height of the stem above the rim of the conical valve cup is critical, for satisfactory assembly of the spray-done. The actuator orifice is 0.51 mm.</p>
Compounding	<ul style="list-style-type: none"> <li>• Add the de-ionized water to a large mixing tank. Dissolve next 4 ingredients. This produces the water-phase. Combine the next 3 ingredients in a smaller tank. This forms the oil-phase. With good agitation, add the oil-phase to the water-phase. This produced a milky, water-in-oil (w/o) emulsion that should be fairly resistant to separation. Agitate the tank during filling, and use a recycling piping system, to prevent phase separation. If the concentrate filler has a small "surge tank" on top, this should also be agitated during filling.</li> <li>• A second source for Oleamide DEA is Croda, Inc. — Incromide OPD.</li> <li>• A second source for Sorbitan Sesquioleate is Uniqema, Inc. Arlacel 83.</li> <li>• A second source for Octoxynol-9 is Henkel (Organic Products Division) — Hynic PE-250.</li> <li>• The Gluteraldehyde (25% Solution in Water) is a strong preservative against possible attack by bacteria or molds. The solution is caustic, corrosive and very sticky. Now sold by the Dow Chemical Company — since they purchased Union Carbide Corporation in 1999.</li> <li>• Formaldehyde (37% in Water) can probably be used as an alternate, at about 0.10%.</li> <li>• Hydrocarbon propellants from 100% iso-butane (Pressure = 2.1 bars at 21°C) to 20% propane and 80% iso-butane, by weight (Pressure = 3.5 bars at 21°C) have been used with this formula. Since the emulsion slowly separates in the aerosol can, labels should direct consumers to "Shake Before Use". It is important to make the water-in-oil (w/o) emulsion form, in order to eliminate any foaming of the spray.</li> <li>• Anhydrous air fresheners, typically using 40% hydrocarbon propellant blends, are easily made, but they are more costly, and very flammable.</li> </ul>
Notes	Fragrance levels vary from about 0.4 to 2.0%, according to intensity and consumer testing.



**Lubricant sprays** are quite popular. The largest selling products also make the promise of “water displacement,” so that metal surfaces will not rust or oxidize on exposure to atmospheric conditions, including salt water. This protection can last for weeks or even months. The sprays also act to loosen rusted bolts. They are used in the home, but also for cars and for industrial applications.

Substance	Supplier	% Wt.
Diocetyl Sodium Sulfosuccinate (100%) as Mackanate DOS-70; see below.		3.000
TLA 620 (Texaco Lubricant Additive)	Texaco Oil Company	2.500
Petrolatum – White or Yellow	Sonneborn Division of Witco Chemical Co.	1.000
Siponic 260 (PEG 6 Iso-lauryl Thioether)	Alcolac Industrial Chemicals Div.	0.500
Hexylene Glycol	Dow Chemical Company	1.500
Ethylene Glycol Monobutyl Ether – As Dowanol EB	Dow Chemical Company	1.500
Mineral Oil		0.400
Fragrance – Optional		0.050
Mineral Spirits – Low odor (Flash Point 43°C minimum)	Open Cup Tester	64.550
Hydrocarbon Propellant Blend (Pressure = 3.5 bars at 21°C.) Could be 38% Propane and 62% Iso-butane, by weight.		25.000
<b>TOTAL</b>		<b>100.000</b>

Can	52 to 65 mm diameter plain inside tinfoil cans. (Many sizes are used.)
Valve	The mounting cup is of plain tinfoil, with either a PE-Sleeve or a polypropylene laminate lining. The stem has 2 x 0.63 mm orifices. The stem gasket is buna. The actuator typically has a 0.51 mm standard orifice, but is generally of a design that can be fitted with an inserted polypropylene extension tube about 10 mm shorter than the can body, but not longer than 150 mm. (This permits very “pin-point” applications, when desired). The capillary extension tube is attached to the can body by using a small rubber band. The valve dip-tube is of standard diameter.
Cover	Normally, a small plastic protective cover-cap, covering only the valve, but full-diameter plastic cover-caps are increasingly seen.
Notes	The first ingredient (used for water displacement) may be purchased as Mackanate DOS-70™ (70% active material), from the MacIntire Group, Ltd. USA, as Triton GR-7M™ (67% active material), from the Rohm & Haas Co. USA and several other large suppliers. The Hexylene Glycol and Ethylene Glycol Monobutyl Ether act synergistically to achieve maximum penetration of rusted screw threads and so forth, but either material can be used successfully without the other, if desired. The hydrocarbon propellant formulas must be used with great caution, for car batteries, electric heater electrodes, ammeter terminals and so forth, where an electric arc could burn a small hole in the can and ignite the contents as they spray out. Some firms have changed their formula to now use non-flammable carbon dioxide as the propellant. This produces a relatively poor, heavy spray, but is very satisfactory when used with the extension tube. Most uses in North America are actually through this extension tube.

The **general purpose cleaners** represent a very large market in North America and Europe. While these products are considered to clean hard surfaces, there are many specialty cleaners, such as glass cleaners, oven cleaners and car tire cleaners that have captured small fractions of this market. There are also disinfectant cleaners, for kitchens and especially for bathrooms, where germ killing is important. The disinfectant cleaner can very often be formulated from ordinary hard surface cleaners by adding small amounts of bactericidal chemicals to the formulas. While general purpose cleaners work well to remove spots and stains from textiles, many specialized cleaners are now designed to do this particularly well. As a rule, these cleaners are sprayed on the spot. Then, after about ten minutes or longer, the textile is washed, removing the stain,

The following formula is effective in removing dirt from hard surfaces. It also contains an optional ingredient, called tetrasodium ethylenediaminetetraacetate (Na<sub>4</sub>EDTA), that can slowly remove discoloring lime deposits from water drippings into sinks and bathtubs. This is done by a process called chelation.

### Hard Surface Spray Cleaner

Substance	Supplier	% Wt.
Linear alcohol propylene glycol ether (9 to 12 mols of ethylene oxide) – As Tergitol 15-S-9	Dow Chemical Company	0.500
Versene 100 (38% Na <sub>4</sub> EDTA in water)	Dow Chemical Company	5.000
Triethanolamine – 85%	Dow Chemical Company	1.000
Propylene Glycol Monobutyl Ether	Dow Chemical Company	4.000
Sodium meta.Silicate 5-Hydrate (Na <sub>2</sub> SiO <sub>3</sub> ·5H <sub>2</sub> O)		0.100
Morpholine – Low odor		0.200
pH Adjuster Ingredients (50% NaOH or 50% Citric Acid in Water; see below) q.s.		
Fragrance		0.100
De-ionized Water		82.100
Hydrocarbon Propellant Blend (Pressure = 3.5 bars at 21°C.) As, 100% Iso-Butane, Could be 18% Propane and 82% Iso-butane, by weight.		7.000
<b>TOTAL</b>		<b>100.000</b>

Can	Usually a 65 mm unlined tinplated can. (Aluminum cans not recommended.)
Valve	Mounting cup is plain tinplate, with a polypropylene laminate inside. The stem orifice is 0.46 mm. The stem gasket is neoprene. The body has a large liquid orifice, and no vapor-tap. The diptube can be the standard diameter, but is preferably a very large (about 7 mm) diameter, to permit several seconds of inverted spraying without releasing the gas. The actuator is a mechanical break-up (standard spray) design, with 0.41 mm orifice.
Cover	Usually a full-diameter plastic design.
Notes	To create a disinfectant cleaner, include 0.40% of BTC 2125M (50% in water) in the formulation. For chemical details refer to the disinfectant-deodorant spray description. After batch completion, adjust the pH to 10.4 to 10.6 (at 25°C) by adding one of the pH adjusting chemicals shown in the formula. Very little is needed. In some countries the disinfectant cleaner is regarded as a pesticide, and made subject to government registration. The spray can be made foamier by shaking the can before use. To remove lime deposits, leave the spray in contact with the lime for an hour or longer, and repeat as necessary for heavier deposits.

The **cookware lubricant** uses a film of lecithin derivative to prevent eggs, cheese, bread or other food products from sticking to heated fry-pans, baking tins and similar cooking surfaces. This avoids the need for large amounts of fats or butter. The spray is more economical, more effective, and adds fewer calories to the cooked foods. This market is about 190,000,000 cans in the USA in 2003, and is said to be growing rapidly as additional firms enter it.

### Cookware lubricant spray

Substance	Supplier	% Wt.
Centrophase 152 (A lecithin derivative)	Central Soya, Inc. USA	7.000
Corn Oil or Soy Bean Oil		70.000
De-ionized Water		4.000
Glycerin – 99.9%		0.650
Butter Flavoring Concentrate – Optional)		0.100
FD&C Yellow No.5 (Food Coloring Agent)		0.020
Hydrocarbon Propellant Blend (Pressure = 3.5 bars at 21°C.) Could be 18% Propane and 82% Iso-butane, by weight.		18.230
<b>TOTAL</b>		<b>100.000</b>

Can	Single-lined tinfoil cans are preferred, in 52 to 65 mm diameters.
Valve	Mounting cup is of plain tinfoil, with polypropylene laminate inside, or PE- Sleeve. Gasket is of Buna. Various (non-vapor-tap) valves can be used, to desired spray pattern. The actuator is a 0.40 mm diameter, mechanical break-up type, often oversize. The dip tube should be aligned to a directional dot on the rim of the valve cup, since the can is often sprayed in a horizontal position.
Notes	This type of formulation is patented in the USA. It exhibits almost no foaming when sprayed onto cold cookware. In North America and parts of Europe hydrocarbons are considered as food additives. But in other parts of Europe hydrocarbons are not permitted to be used in food products. Check with national regulations for more information. Despite the fact that these products are used near gas stove flames, no flammability problems are known. Centrophase C is an alternate for Centrophase 152. Any bleached and derivatized lecithin – from soy beans – should be acceptable.

## Industrial products

Among the most important industrial aerosol products are the **mold release sprays**. They are based on the use of either a lecithin derivative or a silicone fluid as the release agent. Applications include the spraying of mold surfaces in the manufacture of tires and other rubber items.

### **Mold Release Spray**

Substance	Supplier	% Wt.
Dimethylsiloxane Fluid (500 centiStokes viscosity)	Dow-Corning Corp.	2.500
Mixed Hexanes	Shell Oil Company	57.500
Hydrocarbon Propellant Blend (Pressure = 4.8 bars at 21°C.) Could be 35% Propane and 65% Iso-butane, by weight.		40.000
<b>TOTAL</b>		<b>100.000</b>

Can	Tinplate 65 mm diameter can, plain inside.
Valve	Mounting cup of tinplate, with either a polypropylene laminate lining or a PE- Sleeve. For small size sprayings, use a 0.20 to 0.25 mm stem orifice. For larger work, use a 0.33 mm stem orifice. Neoprene stem gaskets are preferred. The body has a large tailpiece orifice and no vapor-tap orifice. Standard dip tubing is used. The actuator should be a mechanical break-up type.
Cover	The cover is usually plastic, fitting over the valve cup but not the top of the can.
Notes	Store 200 liter drums of mixed hexanes out of direct sunlight. Open them in an outside area, since 1 to 2 kg. of extremely flammable vapors will be emitted. Fill the concentrate in an explosion-proof filler, and with a high level of ventilation. Label cans as "Extremely Flammable." Store only in well ventilated warehouses. If the mold-released object is to be painted, change the dimethyl silicone fluid to 231 Fluid, Copolyol 190 or others, preferably as suggested by the silicone supplier. Lecithin derivatives are also used as mold release agents, at about 3.5%. Non-flammable sprays can be produced, using silicone, trans.1,2-dichloroethylene, (boiling point 43.5°C), and about 55% of HFC-134a (CH <sub>2</sub> F-CF <sub>3</sub> ) as the propellant.

### Safe Handling of HAPs in the Laboratory

Cylinders or tanks of hydrocarbon aerosol propellants (HAPs) should be stored outside, except when needed. Then they should be stored in the laboratory exhaust hood. They are normally used to refill glass pressure-burettes or large aerosol transfer cans. In turn, these are used to inject HAPs into aerosol sample dispensers. Nitrogen gas can be used to create extra burette pressure that will facilitate flow into the sample cans. For the transfer cans, mild heating (using warm water), will create the desired flow. The transfer cans have no dip-tube, and their valve stem is connected to the stem of the sample can valve by using a small polyethylene sleeve available from valve companies.

By holding the transfer can above the sample can and pressing it downward, both can valves are opened and liquid propellant flow begins. The weight increase of the sample can is checked, until the desired amount of propellant has been added.

Every aerosol laboratory should have an exhaust hood, preferably at least 2 m wide, and with a duct system leading to the outside air. Gassings and spray-outs of aerosols should be done in this hood. Up to about 4 aerosols at a time may be punctured through the valve cup and slowly de-gassed through the small hole. Any anticipated release of more than about 10 g of hydrocarbon gas should be done in the hood. In most laboratories the hood is run continuously during the working hours. It adds to the general ventilation of air through the laboratory area.

Product development laboratories always have hundreds (even thousands) of aerosols in storage, testing for weight loss, the possibility of corrosion, valve changes and so forth. Some are tested at 40 to 50°C, using heated cabinets. Ventilation should be maintained in these storage areas, to prevent the build-up of flammable concentrations of hydrocarbon gases, and electrical connections should be explosion proof, as it is anticipated that some cans will fail and their entire contents will leak out.

Laboratories should be constructed with at least two exit doors. This will allow workers to leave safely, in case of a serious fire. Every laboratory should have two or more fire extinguishers. Workers should be familiar with how to use them, to put out small fires before they can become larger and more dangerous to life and property.



## ANNEX # 1

## PROPERTIES OF THE HYDROCARBON PROPELLANTS

	PROPANE	ISO-BUTANE	n.BUTANE
Formula	C <sub>3</sub> H <sub>8</sub>	i.C <sub>4</sub> H <sub>10</sub>	n.C <sub>4</sub> H <sub>10</sub>
Molecular Weight	44.1	58.1	58.1
Boiling Point, °C.	-42.1	-11.7	-0.5
Pressure (bars) 21°C.	7.52	2.14	1.17
Pressure (bars) 54.4°C.	17.72	6.69	4.62
Density (g/mL) 21°C.	0.503	0.563	0.583
Flammability Limits in Air (volume-%, 21°C.)	2.2 – 9.5	1.8 – 8.4	1.8 – 8.5
Flash Point, °C.	-104	-83	-74
Solubility in Water (weight-% at 21°C.)	0.006	0.005	0.005



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## About the UNEP DTIE OzonAction Programme

Under the Montreal Protocol on Substances that Deplete the Ozone Layer, countries worldwide are taking specific, time-targeted actions to reduce and eliminate the production and consumption of man-made chemicals that destroy the stratospheric ozone layer, Earth's protective shield. Over 180 governments have joined this multilateral environmental agreement and are taking actions to phase out ozone depleting substances (ODS), which include CFCs, halons, methyl bromide, carbon tetrachloride, methyl chloroform, and HCFCs.

The Parties to this agreement established a Multilateral Fund that provides developing countries with the technical and financial assistance needed to comply with the Protocol. UNEP, UNDP, UNIDO and the World Bank are the Fund's Implementing Agencies.

The objective of UNEP's OzonAction Programme is to assist developing countries and Countries with Economies in Transition to achieve compliance with the control measures of the Montreal Protocol. Since 1991, the Programme has met this goal by strengthening National Ozone Units (NOUS) and facilitating regional and international responses to the ozone depletion challenge by providing the following need-based services:

- Information Clearinghouse, which provides need-based information services that help decision-makers take informed decisions on policies and technologies required to phase out ODS. The clearinghouse has provided over 100 publications and other information aids, including guidelines, videos, CD-ROMs, public awareness materials, a newsletter, sector-specific publications, and a web site.
- National and Regional Training, which builds the capacity of policy-makers, customs officers and local industry to implement national ODS phase-out activities. UNEP promotes the involvement of local experts from industry and academia in training workshops and brings together local stakeholders with experts from the global ozone protection community. To date, OzonAction has conducted 75 training programmes for customs officers and 68 for refrigeration technicians.
- Regional Networking of ODS Officers, which provides a regular forum for those officers to exchange experiences, develop skills, and share ideas with counterparts from both developing and developed countries. Networking helps ensure that NOUs have the information, skills and contacts required to successfully manage their national ODS phase-out strategies. UNEP currently operates 10 regional/sub-regional Networks involving 148 developing and 14 developed countries.
- Refrigerant Management Plans, which provide countries with integrated, cost-effective strategies for ODS phase out in the refrigeration and air conditioning sectors. RMPs assist developing with overcoming the numerous obstacles to phase out ODS in the critical refrigeration sector. UNEP currently provides specific expertise, information and guidance to support the development of RMPs in 74 countries.
- Country Programmes and Institutional Strengthening, which support the development and implementation of national ODS phase-out strategies, especially for low-volume ODS-consuming countries. The Programme has assisted about 105 countries to develop their CPs and 106 countries to implement their IS projects.

In 2002, UNEP restructured OzonAction to better respond to the evolving needs of developing countries during the compliance period. Its overall vision and work strategy was reoriented into the Compliance Assistance Programme (CAP). A major feature of the CAP strategy is to move away from a disparate project management approach towards integrated and direct implementation of the programme using a team of professionals with appropriate skills and expertise. UNEP has now regionalised the delivery of the programme and services by placing its Regional Offices at the forefront to assist the countries in the region.

Primarily funded by the Multilateral Fund, the OzonAction Programme also receives support from the Global Environment Facility, the Government of Sweden, the Government of Finland, and other bilateral sources.

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## About the UNEP Division of Technology, Industry and Economics

The UNEP Division of Technology, Industry and Economics (DTIE) helps governments, local authorities and decision-makers in business and industry to develop and implement policies and practices focusing on sustainable development.

The Division works to promote:

- sustainable consumption and production,
- the efficient use of renewable energy,
- adequate management of chemicals,
- the integration of environmental costs in development policies.

### **The Office of the Director, located in Paris, coordinates activities through:**

- **The International Environmental Technology Centre** - IETC (Osaka, Shiga), which implements integrated waste, water and disaster management programmes, focusing in particular on Asia.
- **Production and Consumption** (Paris), which promotes sustainable consumption and production patterns as a contribution to human development through global markets.
- **Chemicals** (Geneva), which catalyzes global actions to bring about the sound management of chemicals and the improvement of chemical safety worldwide.
- **Energy** (Paris), which fosters energy and transport policies for sustainable development and encourages investment in renewable energy and energy efficiency.
- **OzonAction** (Paris), which supports the phase-out of ozone depleting substances in developing countries and countries with economies in transition to ensure implementation of the Montreal Protocol.
- **Economics and Trade** (Geneva), which helps countries to integrate environmental considerations into economic and trade policies, and works with the finance sector to incorporate sustainable development policies.

*UNEP DTIE activities focus on raising awareness, improving the transfer of knowledge and information, fostering technological cooperation and partnerships, and implementing international conventions and agreements.*

For more information,  
see [www.unep.fr](http://www.unep.fr)



**While most large enterprises that manufacture aerosol products have stopped using CFCs in their manufacturing lines consistent with the Montreal Protocol obligations, there is still a real need for small and medium scale aerosol companies to understand the safety considerations related to the conversion of their plants to alternative propellants. This manual provides plant managers and National Ozone Units with critical information related to the safe conversion of aerosol plants to non-CFC propellants, specifically hydrocarbons. The guide presents detailed information about safety, formula adaptations, and effective destenching methods for aerosol production using hydrocarbon aerosol propellants (HAPs). The goal of this guide is to achieve sustained phaseout by putting Safety First.**

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**Multilateral Fund**  
for the Implementation of the Montreal Protocol

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