

THE GREENING OF AEROSOL PROPELLANTS

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Since the demise of the chlorofluorocarbons (CFCs), the majority of aerosol propellants have been based on light hydrocarbon components such as propane, butane and *iso*-butane. Although combinations of these materials have suitable vapour pressure characteristics they are also classified as Volatile Organic Compounds (VOCs) which contribute both to low-level (tropospheric) ozone and global warming (greenhouse gas) effects.



In addition, the hydrocarbon propellants are highly flammable and have been responsible for many incidents in filling facilities and during their The presence of these residual transportation. hydrocarbons in used canisters poses a significant problem for recycling whilst Volatile Substance Abuse (VSA) is yet another issue affecting aerosol propellants. Indeed, several deaths per year in the UK are associated with the sniffing of aerosol propellants and the release of hydrocarbon-based propellant during designed use is perceived to contribute to problems related to Indoor Air Quality (IAQ). Hydrocarbons are also based on oil, which continues to be geo-politically sensitive and increasingly unattractive economically. The price of crude currently stands at about \$100/bbl and future stocks are likely to diminish as the developing nations continue to industrialise at an alarming rate.

The hydrofluorocarbons (HFCs), which initially replaced the CFCs in many applications, are finding even less favour than the hydrocarbons from the green point of view. These gases have very high Global Warming Potentials (GWPs) and usage of HFCs in aerosols is mostly limited to products which require non-flammable or non-toxic propellants. Many of these applications have already been targeted for phase-out within the European Union. For example, novelty aerosols filled with HFC-134a, as used in party horns or supporter horns, were prohibited in July 2009. Alarmingly, however, such devices have now become commercially available with large-volume, liquid hydrocarbon fillings together with their inherent flame-thrower and solventabusive characteristics.

Compressed gas propellants such as carbon dioxide and nitrogen, on the other hand, are low-cost, lowtoxicity, non-flammable, inert materials ideally suited to the environment. When deployed in aerosol canisters, however, the pressure in the container falls rapidly as the contents are used and causes undesirable changes in the rate of discharge and spray characteristics, which result in low customer appreciation.

To circumvent these problems, gas storage and aerosol dispensing systems have been developed based upon adsorbed aerial gases. One of the least exploited capabilities of activated carbon is its inherent ability to 'condense" or 'immobilize' gases which results in increased gas storage and delivery capacity compared to the usual storage containers. This ability provides other advantages and permits trade-offs in storage system design and hardware.

Ordinarily, gas storage is accomplished by increasing the pressure in a fixed volume container and the amount of gas in the container, under non-extreme conditions, basically follows the ideal gas laws. With activated carbon, not only does 'PV storage occur but, more significantly, the adsorption forces existing in the material's porous structure densify the gas to the point that it achieves a *quasi*-liquid state. Consequently a carbon-filled container can physically deliver more gas than a non-carbon-filled container despite the volume lost to the carbon skeleton.

For the aerosol can and related devices, carbon dioxide is usually the preferred gas for this application when used in conjunction with a selected activated carbon. Nitrogen and other aerial gases, such as air or argon, however, can often be successfully employed.

There are many benefits of employing this combination of materials. Adsorbed aerial gases are non-flammable, non-toxic and environmentally benign¹; they are food compliant and possess little scope for substance abuse or reduction of indoor air quality. The working pressure of a given system can be designed based upon the selection of suitable carbon quantities and gas volumes. Furthermore, the activated carbon used for aerosol applications is manufactured from sustainable resources such as coconut shells, the carbonisation and subsequent activation of which produces more energy than the process itself uses. Provided that the combustible off-gases and by-products are utilised in the carbons' manufacturing process, then no external energy is required. The activated carbon thus derived, ultimately from atmospheric CO₂ (as part of the natural carbon cycle) is stable on the geological timescale and can therefore be considered to be effectively and permanently captured.

¹ Although CO_2 is a greenhouse gas, its deployment in an aerosol canister has, at worst, a neutral effect in terms of global warming because the gas is recovered as a byproduct from a number of industrial processes. For the European market alone, sequestration of the gas in aerosol containers, together with replacement of the hydrocarbon and hydrofluorocarbon gases, is equivalent to removing about 10 million tonnes/year of carbon dioxide from the environment.