

## THE INTERACTION OF FLAMMABILITY AND TOXICITY IN AN AEROSOL PRODUCT

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### Summary

In 1978, changes in federal laws forbid the use of freon<sup>®</sup> propellants in aerosol spray cans. For many products, such as deodorants and household liquids, there were non-aerosol alternatives such as roll-on applicators and pump sprays. Manufacturers of products used in the penetrant system of non-destructive testing did not have this option because one of the products, a developer, requires the fine spray of an aerosol in order to function efficiently.

Faced with this, penetrant material manufacturers split into two groups, one of which adopted carbon dioxide propellants and the other of which adopted hydrocarbon propellants. Since hydrocarbon propellants are flammable and carbon dioxide is not, some users formed opinions about the relative safety of the two systems, and refused to use the hydrocarbon-propelled product.

This paper discusses several safety aspects of the two systems, and concludes that flammability problems are less than toxicity problems, but that neither warrants other than normal precautions.

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### Introduction

In 1978, the Environmental Protection Agency (EPA) took action to ban the use of chlorofluorocarbon (CFC) propellants in aerosol spray cans [1]. Responding to this regulation, manufacturers of products that were popular in aerosol cans sought out alternative methods of dispensing them. Those who elected to continue marketing aerosol cans had their choice of two alternative propellants, liquid hydrocarbons (HC) and high pressure gases, notably carbon dioxide (CO<sub>2</sub>). Manufacturers of a non-destructive test material split in their choice, some manufacturers choosing HC and others CO<sub>2</sub>. Several years after these choices were made, there were allegations that the HC-propelled products were unsafe because of the flammable nature of the propellant. This paper first describes the factors that entered into the choice of propellant for this product and then explores the flammability and toxicological properties of aerosol cans of the product using each propellant.

## The product

The non-destructive test material that is involved has certain performance-characteristic requirements that are important in the discussion to follow. Consequently, a brief explanation of the product will help to set the stage.

A popular method of locating surface cracks and other defects in metals is the penetrant system. This system often uses aerosol cans of these materials for the inspection process. The first material is the penetrant. This is a deep red liquid that is specially formulated to penetrate the surface flaws, no matter how small they are. In practice, it is applied to the metal to be tested so that it covers the entire surface. If there are surface defects, it enters them, as shown in Fig. 1.



Fig. 1. Application of penetrant. Penetrant soaks into flaws.

The second material is a remover, which is used to remove all of the penetrant that is on the surface of the metal without removing that which has entered the flaws. Figure 2 shows that, after the remover has been used, the penetrant remains in the surface flaws.



Fig. 2. Penetrant is removed from the surface but remains in the flaw.

The third material is a developer. This is a fine white absorbent powder suspended in a non-aqueous liquid carrier. When the developer is applied to the surface in a thin even coat, it acts as a blotter. The penetrant in the flaws is drawn into the developer and rapidly spreads away from the crack in all directions. This results in a deep red stain on the white developer background wherever there is a flaw. In order to work properly, the developer must be applied in a very thin, even coat. The importance of this can easily be visualized if one thinks about the amount of penetrant that may be in a flaw that may be only one-thousandth of an inch across and several thousandths of an inch deep. There is so little penetrant in a flaw like this that if the developer is applied too thickly, the penetrant might never diffuse to the surface and the flaw would remain hidden. The trick to a proper inspection is to apply just enough penetrant to form the white background and act as the blotter, but no more. The ideal way to do this is with an aerosol can. Figure 3 shows how the developer works.



Fig. 3. Application of developer. Developer "blots" the penetrant to the surface. The defect shows up in bright red.

For penetrant materials, there are other advantages of aerosol cans. These are:

(a) The materials in the cans remain free of contamination. This is particularly important when specifications require low levels of chlorides, sulfur, and low melting metals.

(b) The containers are self-sealing after each use. This keeps the labels clean, as well as the inspectors' hands and clothes. Penetrants can be very messy and they tend to work their way easily through screw caps that have not been vigorously tightened.

(c) The materials retain their composition. There is no evaporation from the aerosol can.

(d) The excellent application control results in economy of use and minimum clean-up of the surroundings.

(e) Where there might be a safety problem because of exposed flammable penetrant liquids, the use of aerosol cans minimizes the exposure by encapsulating the contents.

(f) Developer application from an aerosol can is almost impossible to duplicate and is a vastly superior method of application. Aerosol spraying of the developer can insure the quality of the inspection.

### The alternative propellants

Both liquid hydrocarbons and carbon dioxide were well known as aerosol propellants at the time a choice had to be made. HC had been introduced in 1933 and, within a few years, various blends of HC were developed which could almost exactly duplicate the pressure characteristics of CFC. The use of HC remained relatively small until 1953 when an aerosol shaving cream was patented and the patent specified CFC as the propellant. In an attempt to get around the patent, HC gained favor. By 1974, more than 55% of all aerosol packages were either partially or wholly propelled by HC [2]. These products included household items, personal care products, paints, and industrial products.

HC are stable, non-corrosive compounds and are essentially odorless liquefied gases. Their toxicity is low and they are environmentally acceptable at the present time. They cost far less than CFC, but more than  $\text{CO}_2$ . HC have good solvent properties, which is an essential attribute for aerosol products in general and penetrant materials in particular. In addition, since HC have lower molecular weights than CFC, and since the volume of gas

produced by the propellant is directly proportional to the molar concentration of the propellant, less HC than CFC is required to produce the same spray characteristics. This enhances the cost advantage, since not only are HC less expensive than CFC, but less HC is required to produce the same result.

When all characteristics are considered, there is a powerful incentive to use HC in place of CFC, since the substitution is simple and results in lower costs. The only characteristic of HC that might be of concern is flammability.

Carbon dioxide has long been used as a propellant, and is well known for this use in seltzer water dispensers. Until recently, however, it has been used only to a minor extent as an aerosol propellant. This is because of certain inherent disadvantages which counteract its appeal as a cheap, environmentally acceptable material that is also non-flammable.

Most of the disadvantages of  $\text{CO}_2$  result from the fact that it is a compressed gas rather than a liquefied gas. When a liquefied gas, such as HC or CFC is in mutual solution with the product to be dispensed, it is maintained under pressure in the can sufficient to keep the propellant liquid. As the aerosol can contents are released through the nozzle into atmospheric pressure, the propellant immediately boils and evaporates into the gas phase. Since the propellant and the product are discharged from the nozzle in the mutual solution, the evaporation of the propellant breaks the liquid product up into tiny droplets, or aerosols.

A second advantage of a liquefied propellant is that the pressure within the aerosol can remains essentially constant from the first use of a full can to the last drops sprayed. This happens because, as the contents are sprayed, the volume in the can is refilled with propellant vapor that evaporates from the liquid propellant. There is more than sufficient liquid propellant for this purpose, and the equilibrium pressure in the can is essentially the same from start to finish. Thus the spray characteristics remain constant, which is essential in certain products, such as paints, and desirable in all products.

A third advantage is that the adequate reserve of propellant allows the nozzle and delivery tube to be cleaned without any subsequent loss in pressure. The can is inverted, so that the delivery tube opening is now projecting into the propellant gas phase, and then the nozzle is depressed. Whatever liquid is in the tube and nozzle is sprayed, followed by a spray of pure propellant gas that cleans the nozzle.

Carbon dioxide cannot be liquefied in an aerosol can, and thus these advantages are lost. While HC and the aerosol product are usually mutually soluble in all proportions, this is not true of  $\text{CO}_2$  and the product.  $\text{CO}_2$  is soluble in most liquids, with the degree of solubility being expressed as the Ostwald coefficient, which is the ratio of the volume of dissolved gas per volume of liquid. Further, as the gas pressure is increased, the amount of gas that is dissolved also increases. Aerosol cans are designed for a maxi-

imum internal pressure of about 100 psi, and, at this pressure, a total of about 13 g of CO<sub>2</sub> can be charged to the can. These 13 g will produce a maximum volume of about 0.25 ft<sup>3</sup> of gas to break up the product into droplets. In contrast, the HC-propelled can produces about six times as much gas and is far more efficient at breaking the product into droplets.

Because there is no CO<sub>2</sub> liquid in equilibrium with the CO<sub>2</sub> gas in the aerosol can, the propellant pressure obeys the gas law. The pressure begins at about 100 psi, and when the can is almost empty it has dropped to about 45 psi. This drop in pressure changes the spray characteristics from a high spray rate to a lower spray rate, and the droplet size becomes coarser.

Finally, if an attempt is made to clear the valve by inverting a CO<sub>2</sub> propelled can, the results are invariably a complete loss of pressure, since there is no liquid propellant to replace that which has escaped.

Carbon dioxide has advantages that are quite attractive. It is the least expensive aerosol propellant. It is odorless, colorless, low in toxicity, non-flammable and environmentally acceptable. Also, extreme drops in temperature do not affect the pressure of a CO<sub>2</sub>-propelled aerosol as much as they affect an HC-propelled aerosol.

### **The choices made**

As mentioned in the Introduction, some manufacturers of penetrant materials chose CO<sub>2</sub> as a propellant and others chose HC. The reasons behind the choices may be complex and may have involved trade-offs of factors not discussed in this paper. But certainly these trade-offs included balancing the superior performance of HC propellants against their flammability, and the non-flammability of CO<sub>2</sub> propellants against their disadvantages as a propellant. For whatever reasons, the industry divided into two camps.

After a period of time, it became clear that some users of the developer rejected HC-propelled cans based on allegations that they were dangerous to use because of their flammable nature. As might be expected, the manufacturers of CO<sub>2</sub>-propelled developer did nothing to dispel the allegation and may have even spread it further.

### **Factors affecting safety**

The thrust of this paper is to put the flammability aspects of the HC-propelled developer into context with other safety aspects of the product in the can, and particularly to compare the overall safety of the two different systems. To do this, we must examine the product in more detail.

#### *Aerosol can contents*

Figure 4 illustrates what is in an aerosol can of developer. The powder is inert, non-flammable, and non-toxic. There is no essential difference

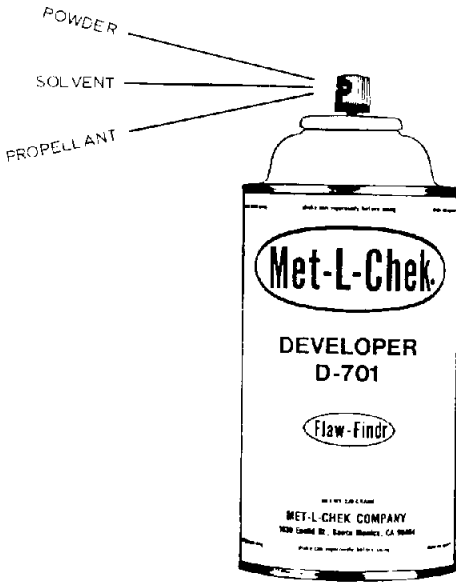


Fig. 4. Aerosol can contents.

among various manufacturers' products with regard to these characteristics.

The solvent keeps the powder wet, helps the penetrant migrate from the flaws, and mixes uniformly with liquid propellants.

The most common and popular aerosol developers use chlorinated hydrocarbons as the liquid solvent. These liquids are common industrial chemicals that are inert to both the aerosol cans, the developer powder, and the parts to be inspected. They are good solvents and easily dissolve penetrants. The chlorinated hydrocarbons have relatively high evaporation rates, which also qualify them for the purpose. After the parts are sprayed, the coating remains wet for a sufficiently long period to insure a smooth even coat. While wet, the solvent properties dilute the penetrant so that it migrates out of the cracks. Finally, the chlorinated hydrocarbon evaporates and the dry coating is left as a white powder which absorbs and magnifies the penetrant indications.

Several types of chlorinated hydrocarbon have been used for developer solvents. Methyl chloroform (or 1,1,1-trichloroethane) is a popular liquid today, and is used either wholly or partly by most developer manufacturers. When used with HC propellants, they are mutually soluble, and the spray from aerosol cans contains droplets that are initially part methyl chloroform, part HC, and part developer powder. The HC almost instantly flashes from a liquid to a vapor and, in so doing, produces the very fine mist-like spray that is desired in applying the developer.

Methyl chloroform can be used with  $\text{CO}_2$  propellants, but it is more commonly mixed with methylene chloride, another chlorinated hydrocarbon

industrial solvent. This is done because the compressed CO<sub>2</sub> does not have a liquid phase like the HC, and this lack of the liquid contributes to undesirable performance characteristics such as poor atomisation, changing pressure over the life of the can, and easy loss of propellant power before the can has been emptied. Attempts to cope with these failings of the single-phase CO<sub>2</sub> rely upon dissolving more of the gaseous CO<sub>2</sub> in the liquid carrier. Methylene chloride dissolves about 25% more CO<sub>2</sub> [3] than does methyl chloroform, so it is used to augment the primary carrier solvent.

Both methyl chloroform and methylene chloride are toxic chemicals. They must be used with adequate ventilation and OSHA has established threshold limit values (TLV) for them. The TLV of methyl chloroform is 350 parts per million (ppm) of air and the TLV of methylene chloride is 500 ppm [3].

The propellant also serves several purposes. Primarily, it provides the pressure required to eject the developer from the can. But, as explained above, the propellant also acts to develop the fine mist-like spray that is a basic characteristic of aerosol cans. HC propellants are miscible with the carrier liquid in all proportions and are liquid when confined within the can at their equilibrium pressure of about 45 p.s.i. When sprayed, the HC flashes to a gas almost instantaneously to produce fine droplets and a smooth even coat of developer.

HC are flammable gases, with a lower flammability limit of 20,000 ppm [2] or 2% in air.

Carbon dioxide is not present as a liquid in aerosol cans, and is not miscible with the carrier liquid. It has some solubility and, as explained, this limited attribute is exploited by using methylene chloride. While HC propellants serve the dual function of providing pressure and producing a fine spray, CO<sub>2</sub> propellants mostly provide only the pressure. The spray characteristics of CO<sub>2</sub>-propelled developers rely mainly upon the design of the valve that is used.

Carbon dioxide is not flammable. It is present in normal air at about 300 ppm concentration. It has adverse affects on breathing at higher concentrations and has a TLV of 5000 ppm [4].

Table 1 summarizes the contents of both types of aerosol can, together

TABLE 1

Aerosol can contents

CO <sub>2</sub> -propelled	HC-propelled
Powder (inert)	Powder (inert)
Methyl chloroform (350 ppm)	Methyl chloroform (350 ppm)
Methylene chloride (500 ppm)	HC (20,000 ppm)
CO <sub>2</sub> (5000 ppm)	

with the concentrations of each ingredient that indicate either the TLV or the lower flammability limit.

### Safety aspects

Both types of developer have the potential for a problem. The CO<sub>2</sub>-propelled can could cause toxicity problems with the methyl chloroform, the methylene chloride, or the CO<sub>2</sub>. The HC-propelled can could cause a flammability problem with the HC or a toxicity problem with the methyl chloroform. Whether any of these problems would occur, or which would occur first, depends upon how the can is used.

To illustrate this, let us suppose that a full can of the developer is completely sprayed into a closed space with no ventilation. The volume of the space will determine the concentration of the various ingredients and whether a problem occurs. Table 2 lists these volumes, expressed as the dimensions of a room that is 8 ft high. Note that the primary danger from either can is a toxicity problem resulting from the solvent. Note also that the danger of HC flammability is essentially no worse than the toxicity of the CO<sub>2</sub>.

TABLE 2

Danger points when a complete can is expelled

CO <sub>2</sub> -propelled	HC-propelled
Powder (none)	Powder (none)
Methyl chloroform (18 ft × 18 ft room)	Methyl chloroform (14 ft × 14 ft room)
Methyl chloride (15 ft × 15 ft room)	HC (2.5 ft × 2.5 ft room)
CO <sub>2</sub> (2.5 ft × 2.5 ft room)	

Table 3 rearranges this information by describing what kind of a situation would exist if the flammability point of an HC-propelled can was reached. In summary, it concludes that the user of the can would have to expose himself to at least 26 times the OSHA allowable level of the solvent in

TABLE 3

Concentration of other ingredients at HC flammability limit

CO <sub>2</sub> -propelled	HC-propelled
Powder (none)	Powder (none)
Methyl chloroform, 42 × OSHA limit	Methyl chloroform, 26 × OSHA limit
Methylene chloride, 31 × OSHA limit	HC, flammable
CO <sub>2</sub> , 91% of OSHA limit	



order to have the danger of fire. Using a CO<sub>2</sub>-propelled can in the same situation results in a dual overexposure of methylchloroform and methylene chloride, the first by 42 times the OSHA limit, and the second by 31 times the OSHA limit.

There are no publicized accidents of either toxicity or flammability from these cans, and it is easy to see why. The conditions that would have to be met to cause such a problem are so remote from the usual conditions of use of these materials that we never hear of either a poisoning incident or a flammability incident. However, given the fear of flammability, it should be noted that toxicity problems are far more likely to occur, particularly with the CO<sub>2</sub>-propelled developer.

One more bit of context is relevant. The most common propellant in use in this country is HC. Over 12 billion ( $12 \times 10^9$ ) of these cans have been sold since 1978, and they contain hairspray, deodorant, paint, insecticide, lubricant and the like. Because some of these products contain alcohol or petroleum solvents, they are far more flammable than the developers in this discussion. Yet these have the approval of EPA, OSHA, and the Consumer Product Safety Commission. The reason is that they are safe, so safe that they are used in virtually every home and workplace in America without hazard. With the safety record that exists, one can only conclude that claims of danger due to HC propellants are exaggerated, and that the probability of an accident in ordinary use is very low. In addition, the potential for a problem is probably not significantly different than that associated with a CO<sub>2</sub>-propelled can.

## References

- 1 Federal Register, March, 17, 1978.
- 2 P.A. Sanders, Handbook of Aerosol Technology, Van Nostrand Reinhold, New York, 1979.
- 3 Baron-Blakeslee, Inc. and others, Material Safety Data Sheets, based on OSHA criteria.
- 4 M.A. Johnsen, The Aerosol Handbook, 2nd edn., Wayne Dorland Company, Mendham, NJ, 1982.