

HEXAFLUORINE FOR EMERGENT DECONTAMINATION
OF HYDROFLUORIC ACID EYE/SKIN SPLASHES

Hall AH*, Blomet J**, Gross M+, Nehles

J++

* Toxicology Consulting and Medical
Translating Services, P.O. Box 24, Mile 5.0
Pass Creek Road, Elk Mountain, WY 82324, USA
**Laboratoire PREVOR, Valmondois, France
+R. Woeste and Co., Velbert, Germany
++ Manesmann Hoesch Praziorohr, Remscheid,

Germany

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F95760, Valmondois, France

ABSTRACT

Introduction: Hexafluorine is a novel eye/skin decontamination compound produced by Laboratoire PREVOR in France. It is an amphoteric, hypertonic chelating agent specifically designed to detoxify hydrofluoric acid (HF). Hexafluorine has chemical bond energy greater than those of eye/skin tissue receptors and does not produce a significant exothermic reaction with release of heat which could further damage exposed tissues. Case Reports: 1) a worker fell into a bath containing 1,505 L of water, 30 L of concentrated hydrochloric acid, and 233 L of 59% HF, immersing the entire body and face. Hexafluorine was immediately used for decontamination by co-workers and a regular water eyewash was also used. Only minor burns developed on the back and abdomen. There was a significant corneal burn of the left eye, while the right eye remained normal. 2) In a facility producing stainless steel for construction and machine tools which uses a chemical dipping bath containing nitric and hydrofluoric acids, a worker sustained an eye splash with 38% HF, rinsed the eye immediately with Hexafluorine, did not develop any eye injury, and returned to work the next day. 3-5) 3 other cases of workers with 20% HF skin splashes who did not develop any burns after decontamination with Hexafluorine have been reported to Laboratoire PREVOR. Discussion:

Hexafluorine has been compared with plain water and calcium gluconate decontamination in rabbits and rats, and was more efficacious. Water rinsing at 10 L/minute for 5 minutes was not effective, and water rinsing plus calcium gluconate inunction was not as efficacious as Hexafluorine, which has an affinity for hydrogen and fluoride ions approximately 100 times as great as that of calcium gluconate in vitro. Conclusion: Hexafluorine is currently the best alternative for decontamination of HF eye/skin splashes.

Key Words: Hydrofluoric acid; Hydrofluoric acid, burns; Hydrofluoric acid, decontamination;

Hydrogen fluoride; Hydrogen fluoride, burns; Hydrogen fluoride, decontamination; Hexafluorine

INTRODUCTION

Hydrofluoric acid (HF) is an aqueous solution of hydrogen fluoride (Hathaway et al 1996). Hydrogen fluoride is a gas which liquifies at 19.5 degrees C (Hathaway et al 1996). HF

has a wide variety of industrial applications including use as a catalyst for producing high-octane gasoline, in the production of fluoride compounds, for removing sand from metal casings in the petroleum industry, as the aqueous form for polishing, etching, and frosting glass, in the ceramics industry, and in the semiconductor industry for etching silicon wafers (Hathaway et al 1996; El Saadi et al 1989; Upfal and Doyle 1991). Dilute solutions containing 6-11% HF are also available as consumer products for removal of rust stains (El Saadi et al 1989).

Hydrofluoric acid in anhydrous or concentrated forms is a severe corrosive substance, but is a weak acid which remains relatively non-ionized in dilute solutions and rapidly penetrates lipid barriers into deep tissue layers following skin or eye contact (Upfal and Doyle 1991; Carlton and Vance 1998). Hand injuries are particularly problematic, as fingertip ulceration, dissolution of underlying bone, and even loss of digits may occur.

Severe signs and symptoms or deaths are generally due to the systemic toxicity of HF which binds to calcium and magnesium resulting in hypocalcemia and hypomagnesemia causing life-threatening cardiac conduction disturbances, dysrhythmias, and cardiac arrest (Upfal and Doyle 1991; El Saadi et al 1989; Edelman 1986; Mayer and Gross 1985). In addition,

significant hyperkalemia and metabolic acidosis leading to cardiac arrest and other systemic effects have been reported in fatal exposure cases (Tepperman 1980; Chan et al 1987). For HF dermal or eye exposures, a number of sources recommend immediate and prolonged initial irrigation with water for 15 to 30 minutes (Ellenhorn 1998; Carlton and Vance 1998; Upfal and Doyle 1991; Edelman 1986; NIOSH 1997). However, the novel HF decontamination compound Hexafluorine produced by Laboratoire PREVOR in France may be a much more efficacious alternative. Hexafluorine is an amphoteric, hypertonic chelating substance specifically designed to decontaminate HF. It has a chemical bond energy for HF greater than those of eye/skin tissue receptors and does not result in a significant exothermic reaction with release of heat which could further injure exposed tissues.

MATERIALS AND METHODS

CASE REPORTS

Case No. 1:

A worker fell into a bath containing 1,505 liters of water, 30 liters of concentrated hydrochloric acid, and 233 liters of 59% HF, immersing the entire body and face. Hexafluorine was immediately used for decontamination by co-workers and a regular water eyewash was also used. Only minor burns developed on the back and abdomen. There was a significant corneal burn of the left eye, while the right eye remained normal.

Case No. 2:

In a facility producing stainless steel for construction and machine tools which uses a chemical dipping bath containing nitric and hydrofluoric acids, a worker sustained an eye splash with 38% HF, rinsed the eye immediately with Hexafluorine, did not develop any eye injury, and returned to work the next day.

Case Nos. 3-5:

Three other cases of workers exposed to HF and decontaminated with Hexafluorine have been reported to Laboratoire PREVOR (Josset et al 1992). All three workers had skin splashes with 20% HF involving less than 5% of the total body surface area. When immediate Hexafluorine decontamination was done, no burns

developed.

IN VITRO DATA

To simulate the effects of decontamination without flushing, 10 milliliters of 0.1 Normal HF (0.2%) were placed in a beaker and water, 10% calcium gluconate, or Hexafluorine were added (Josset et al 1992). The pH and pF (pF = negative logarithm of the fluoride ion concentration) were measured.

Water had little effect on either pH or pF. Both calcium gluconate and Hexafluorine absorbed or neutralized the hydrogen ion, although Hexafluorine bound the hydrogen ion 100 times greater than calcium gluconate (final pH was 6.5 with Hexafluorine versus 4.5 with calcium gluconate). As the causticity limit of hydrogen ion is approximately pH 5.5, caustic injury may still occur despite calcium gluconate use.

After calcium gluconate addition to the beaker, the final pF was 3. With Hexafluorine addition, the final pF was 6. As the toxicity limit is a pF of less than or equal to 5, fluoride tissue toxicity may occur despite use of calcium gluconate but should not occur following use of Hexafluorine .

EXPERIMENTAL ANIMAL DATA

In the following experiments, all applicable ethical research standards and regulations pertaining to animal experiments (anesthesia, hygienic conditions, animal maintenance) were followed (Josset et al, 1992). In both studies, 70% hydrofluoric acid (Atochem) was utilized.

Rabbits

In 120 New Zealand albino white rabbits divided into 6 groups of 20 rabbits each, three types of irrigation were tested following burns created by application of a 1 centimeter diameter piece of filter paper saturated with 70% HF (less than 1% total body surface area). After application of the HF-saturated filter paper, irrigation with water at an approximate rate of 10 liters/minute for 5 minutes, irrigation with water at a rate of approximately 10 liters/minute for 3 minutes followed immediately by inunction of 2.5% calcium gluconate gel, or irrigation with Hexafluorine at a rate of approximately 0.2 liter/minute for 3 minutes (500 milliliters over 3 minutes) were done.

Observations of the exposed areas were made at 10 minutes, 1 hour, 2 hours, and then every 24 hours for 6 days. Burns were classified as no burn, visible burn, extensive burn, or severe burn.

With water irrigation alone, burns were visible at 10 minutes, extensive at 1 hour, and severe at every observation point from 2 hours through day 6. With water irrigation plus 2.5% calcium gluconate gel inunction, there were no burns at 10 minutes, 1 hour, or 2 hours, but burns were visible on days 1 and 2, and were extensive on days 3 through 6. With Hexafluorine irrigation, there were no burns at any observation time from 10 minutes through day 6.

Rats. In this experiment, 62 adult male Charles River Wistar rats were divided into groups of 20 animals each (2 unexposed controls) and had burns induced by application of a 1 centimeter square piece of filter paper saturated with 70% HF (0.6% of total body surface area). Following HF application, 20 treatment animals in each group then had one of the 3 types of decontamination described above. Serum calcium levels were sequentially measured to determine if hypocalcemia occurred and if there were differences in the pattern over time in animals having the three different types of decontamination.

With water irrigation alone and water irrigation plus calcium gluconate inunction, hypocalcemia was present between 10 minutes and 1 hour, and at 4 hours there was a more pronounced hypocalcemia which had somewhat resolved at 24 hours. Serum calcium levels then returned to normal over 5 days. With Hexafluorine irrigation, the more pronounced decrease in serum calcium levels was not observed at 4 hours and levels were similar to control values at 5 days.

DISCUSSION

In 1997, 1,109 cases of hydrofluoric acid exposure were reported to Poison Control Centers in the USA (Litovitz et al 1998). The majority of exposed persons were adults (864/1,109; 78%) and most exposures were unintentional (1,091/1,109; 98%). Of these patients, 658 (59%) were treated in a health care facility, 772 (70%) developed symptoms ranging from minor to severe, and there were 2 deaths.

The rapidity of symptom onset following dermal exposure is dependent on the HF concentration. Dermal exposure

to solutions of less than 20% concentration sometimes results in a delay in symptom onset of up to several hours (El Saadi et al 1989). The risk of severe systemic effects seems greatest with exposure to 50% or greater concentrations of HF on 1% of the total body surface area or more and any dermal exposure on greater than 5% of the total body surface area (Upfal and Doyle 1991).

Once HF skin burns have developed, a variety of treatments have been advocated including inunction of calcium gluconate gel, topical application of magnesium oxide paste, iced benzalkonium chloride soaks, and more invasive treatments such as local injection of calcium gluconate, surgical excision of effected areas and removal of fingernails if subungual exposure is present, and intravenous (using the Bier block technique) or intra-arterial administration of calcium gluconate (for finger/hand burns) (Browne 1974; Edelman 1986; El Saadi et al 1989; Upfal and Doyle 1991; Henry and Hla 1992; Siegel and Heard 1992; Vance et al 1986; Velvart 1983). Other surgical burn care may also be required (Browne 1974; Upfal and Doyle 1991).

Allowing an HF dermal burn to develop following exposure results in patient discomfort or pain, often severe (Carlton and Vance 1998). Systemic absorption of more concentrated HF solutions may result in life-threatening toxicity (Upfal and Doyle 1991; El Saadi et al 1989; Chan et al 1987; Edelman 1986; Tepperman 1980). The above treatments can be used safely, but have potential complications. Beyond safety measures to prevent HF skin splashes from occurring, immediate skin decontamination with the most efficacious decontamination solution available should be done.

Eye exposure to HF may result in initial lacrimation, conjunctival irritation, and pain. Subsequent tissue penetration may result in severe damage with corneal erosions and necrosis, corneal opacification, and corneal vascularization and scarring; penetration of the globe may sometimes occur (Carlton and Vance 1998; Sadove et al 1990; Bentur et al 1993; McCulley et al 1983; Hatai et al 1986). Water irrigation and irrigation with calcium gluconate solutions have been proposed (Upfal and Doyle 1991; Bentur et al 1993). Prevention with safety measures is imperative, but when splashes do occur immediate irrigation with the most efficacious decontamination solution available should be done.

CONCLUSION

Based on the data presented here, Hexafluorine appears to be the most efficacious compound currently available for immediate decontamination of hydrofluoric acid eye/skin splashes and can prevent or significantly decrease the extent of HF burns.

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