Journal of Industrial and Engineering Chemistry 18 (2012) 1529–1539

Contents lists available at SciVerse ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Review

A review of hydrofluoric acid and its use in the car wash industry

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ARTICLE INFO

Article history:
Received 22 October 2011
Received in revised form 28 February 2012
Accepted 2 March 2012
Available online 10 March 2012

Keywords:
Hydrofluoric acid
Car wash
Automobile
Brake and road dusts
Hypocalcaemia
HF alternatives/replacement

ABSTRACT

Hydrofluoric acid (HF) is a common ingredient in car wash cleaning solutions mainly because it is highly effective and relatively inexpensive. Particulate matter from brake pads and discs, tire wear, and abrasion of road surface accumulated on the exterior of automobiles are aggressively removed with the use of car wash cleaning solutions containing HF. The unique properties of HF to dissolve silica, concrete, most metals, and metallic oxides cause effective breakdown of rust, road dust, and grime on automobiles. However, HF is a very caustic and a highly toxic substance. Due to hazards associated with the storage, use, and exposure of HF to humans and the environment, there is a need to find safe, yet equally effective alternatives to HF as a cleaning agent. Improvements in cleaning processes, development of available technologies, and utilization of cleaning products containing natural and various benign polymers and surfactants are healthy and environmentally sound alternatives to HF for car wash applications. However, these alternatives may not be as effective as HF. Efforts geared towards finding a replacement for HF remain a challenge, but the outcome would render several benefits to the car wash industry, including abating pollution and providing a safer working environment for everyone.

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1. Introduction

Hydrofluoric acid (HF) is a valued chemical in the academic, domestic, and industrial settings, being a precursor to numerous products and materials [1]. Large quantities of crude HF were first prepared by Carl Wilhelm Scheele in 1771 [2]. In the late 1800s and early 1900s, HF was utilized for glass etching, foundry scale removal, and sodium fluoride compound and high-octane fuel productions. The results of these applications have given birth to the use of HF as a primary ingredient in car wash cleaning solutions. Historically, most car wash cleaning products are based on detergents containing mild alkalis and dilute HF, formulated to loosen and eliminate dirt and grime on automobiles [3]. As the global automotive industry grew, there had also been activities

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1226-086X/$ – see front matter
doi:10.1016/j.jiec.2012.03.001

involving the use of HF in professional car wash businesses, including those in car service and maintenance sector, due to the need for cheaper, more effective, industrial strength cleaning solutions. A clean automobile has become a necessity since then as more people washed their automobiles on a regular basis. Today, it is estimated that at least 50 car wash systems are installed annually by the United States and European manufacturers [4].

Since 1939, professional car wash businesses offer consumers an easy, time-saving, and practical way to wash dirt and grime from their automobiles [5,6]. Cleaning an automobile basically consists of the actual removal of oil and dirt, and then treatment to provide protection [7]. Degreasing solvents and cleaning agents remove traffic grime and particulate matter on automobiles, then the subsequent application of wax polishes and protects coatings. The operation of professional car wash facilities, both traditional and modern, generally falls under the following categories: hand car wash, self-service, in-bay automatics, tunnel washes, chemical car wash, and steam car wash facilities [8]. In the conveyor-operated car wash, the car moves by means of a conveyor through a tunnel and is washed by either friction or frictionless system. The frictionless system uses high-pressure nozzles to spray the car with cleaning solutions, whereas in the friction system, a series of brushes wash the car when moving through the system. In the in-bay automatic process, the car remains stationary while a machine moves back and forth as it washes over the vehicle. In self-service stations, the customer is responsible for washing the car using a low-pressure brush or hoses with nozzles that dispense either water or the cleaning solution at controllable amounts and pressures. In both conveyor and in-bay automatic systems, workers are needed to physically spray some chemicals on the car. The ideal car wash cleaning solution removes road dust, rust stain, dirt, films from brakes, and grime from the automobile with minimal effort. HF-based car wash cleaning solutions accomplish this task effortlessly.

Along with the popularity of HF comes the complexity of its regulatory laws due to its harmful effects to humans and the environment. Significant local and systemic toxicity may occur from HF by inhalation, oral, ocular, and dermal exposures during washing. Therefore, there have been strong efforts in the automotive industry to develop safer car wash cleaning solutions and to improve available car wash technologies [9]. As a result of this move, the number of professional car wash facilities that use HF has declined and car wash operators are required by law to reuse and pre-treat their effluent wastewater and maintain wastewater discharge permits [10]. In recent years, these facilities use water reclamation systems and energy usage reduction technologies. However, 44.5% of car owners in the U.S. alone (approximately equivalent to 61 million passenger cars in 2008 data [11]) still prefer driveway or backyard washing and at least 75% of all cars are washed at home at least once a year [10]. This is a concern since HF is still being used as an ingredient in a number of common commercial cleaning solutions. Categorized as an unregulated car wash facility, driveway washing also generates hazardous wastewater that ends up in the storm drain and could potentially contaminate ground and surface water. Hence, some state and local institutions have begun campaigns to encourage consumers to utilize regulated but costly professional car wash facilities as opposed to driveway and mobile charity car washing by hand.

To date, there are no academic institutions or public laboratories that directly focus their research on the fundamental chemistry of HF for car wash applications. This is not surprising not only because of the unusual and difficult nature of HF systems but also because almost all the extensive research and development of the alternatives to HF-based cleaning products are being done by chemists in industry for commercial use. However, this does not mean that there are no research facilities (both academic and industrial) capable of undertaking such a research effort.

In this literature review, we provide background information on the sources, global production, and several uses of HF. The physicochemical properties of HF, toxicity, harmful effects to humans and the environment, and regulations pertaining to its use, are also reviewed. We also highlight materials selection and storage guidelines for HF, car wash cleaning formulations, and sources and properties of non-exhaust particulate matter that accumulate on automobiles from road traffic. Primary attention is given to the use of HF in car wash cleaning applications including an explanation of its effectiveness against typical brake and road dusts. In the last section, recommendations and a summary of possible candidates for HF replacement that are found in domestic and industrial settings are given.

2. Sources of hydrofluoric acid

The mineral fluorite, commonly called as fluorspar (CaF_2), is the important starting material for the production of hydrogen fluoride, fluorine, and sodium fluoride [12]. Other alternative starting materials include fluorapatite ($Ca_5(PO_4)_3F$) and cryolite (Na_3AlF_6). Hydrogen fluoride, the most important manufactured compound of fluorine, is also generated upon combustion of many fluorine-containing compounds such as products containing Viton® and polytetrafluoroethylene (Teflon®) parts [13]. Fluorite is found as deposits in various parts of the world, notably in China, Germany, Austria, Switzerland, England, Norway, Mexico, Canada, and Kenya [14]. In the U.S., commercial mining for the production of fluorite was conducted in Illinois until 1995. As of today, the National Defense Stockpile is the source for all domestic U.S. supplies of fluorite. Small quantities of synthetic fluorite are also produced from industrial waste streams [15].

HF is produced from anhydrous hydrogen fluoride, a colourless gas or liquid at ambient temperature. HF is also a product of hydrolysis by moisture of fluorine-containing compounds such as carbonyl fluoride, BF_3, PF_5, SiF_4, SF_4, and PF_3 from volcanic emissions [16]. Ocean spray and dust from the weathering of fluoride-containing rocks and soils, and anthropogenic activities are the other sources of airborne fluoride compounds [17,18].

When anhydrous hydrogen fluoride is released into the atmosphere, contact with water vapour leads to immediate fuming and formation of a white mist [19]. Anhydrous hydrogen fluoride is normally manufactured at a purity level of 99–99.9%, whereas HF is primarily produced commercially as a 70% solution [20]. Electronic and reagent grades HF of 5–52% are also manufactured industrially [20]. Essentially all anhydrous hydrogen fluoride is manufactured worldwide by the chemical reaction of CaF_2 and H_2SO_4, owing to Gay Lussac and Thernard, the first chemists who managed to obtain pure form of HF in 1809 [21]. When combined in heated kilns at 538 K, CaF_2 and H_2SO_4 react to produce anhydrous gaseous hydrogen fluoride and solid $CaSO_4$ as shown in Equation 1 [22].

$$CaF_{2(s)} + H_2SO_{4(l)} \rightarrow 2HF_{(g)} + CaSO_{4(s)} \tag{1}$$

This process utilizes acid-grade fluorite ($\geq$97.5% CaF_2), which is distilled with concentrated H_2SO_4. Hydrogen fluoride leaving the reactor is purified by distillation after being condensed. HF is then rapidly obtained by dissolving the anhydrous hydrogen fluoride in water.

Hydrogen fluoride is also produced as a by-product of the extraction of the fertilizer precursor H_3PO_4, which is obtained from the mineral apatite ($Ca_5(PO_4)_3(F,Cl,OH)$) [13]. Acid digestion of fluoroapatite in apatite sources releases a gaseous stream consisting of hydrogen fluoride, SO_2, H_2O, and particulate matter.