The Harshaw Chemical Company:
As Seen Via One Great Series of Stories

Morgan Cox

INTRODUCTION

This is the story, or rather a short series of stories, about a mid-sized American chemical company, namely the Harshaw Chemical Company, founded in the 1890s. Some of the more significant technical innovations and contributions of this company must be chronicled here or else they will be buried and lost to history forever. Some of the key scientists, business contributors, inventors and technical consultants for the company deserve more recognition than this article can possibly document. The Harshaw Chemical Company was based in Cleveland, Ohio.

This is truly an American success story replete with shorter stories, anecdotes and a touch of humor. Through multiple acquisitions by other companies, Harshaw has lost its identity, but certainly not its place in the history as a vital part of the American chemical industry.

This article is dedicated to some of the many people who made this company a leader in its industry throughout its existence. In particular, the author would like to single out two distinguished gentlemen who graciously narrated much of the background and substance for the content of this story: Carl F. Swinehart, PhD, and David A. Hammond, PhD, took time in late 1999 and late 2003 to provide many of the details in this work.

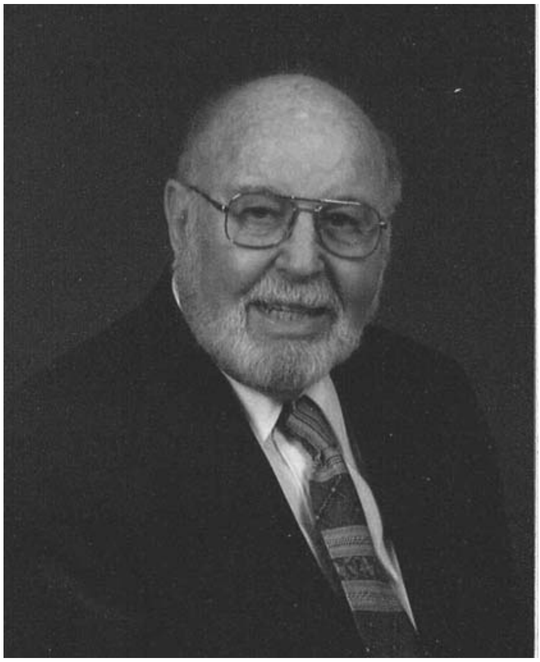
Carl Swinehart began his career with Harshaw Chemical in 1932, and consulted for the company and its successors into the late 1990s! David Hammond began his career with Harshaw in 1950, and consulted weekly until 2000 with Bicron, a survivor of the Harshaw heritage! Both Doctors Swinehart and Hammond earned their doctoral degrees from Western Reserve University in Cleveland.

To bring the accomplishments of these two outstanding scientists into perspective, not only is their loyalty and longevity noteworthy, but, Dr. Swinehart is the holder of 29 US patents (including three in 2001!) and Dr. Hammond holds another 5! The US patent issued to Dr. Swinehart in 1947—for the fluorine cell—is among the most important of these. We will demonstrate later in this work why that patent was so crucial for the United States of America.

Among the other great people who have contributed and otherwise distinguished themselves with Harshaw and left us, is Elmer C. Stewart. Stewart, himself was a graduate chemist, and was Vice President and General Manager of the Crystal and Electronic Products Department for Harshaw for some twenty years. Under Stewart's management and leadership, Harshaw became the worldwide leader in the development and supply of commercially available scintillation radiation detectors, namely with sodium iodide (thallium-activated) and others, thermoluminescence (or TL) materials such as lithium fluoride, calcium fluoride and related thermoluminescence dosimetry (or TLD) instruments and systems. The Crystal and Electronics Department often engaged the expertise of Nobel Laureate, Dr. Robert Hofstadter of Princeton and Stanford Universities, in developing the scintillation detector program and business. Similarly, the Department also called on outstanding consultants such as Drs. James Schulman of the Naval Research Laboratory (NRL), John Cameron of the University of Wisconsin and Herb Attix of both NRL and the University of Wisconsin in developing the successful TLD program. Elmer Stewart left us suddenly in 1986, a sad victim of cancer at age 67.

Dr. Carl Swinehart

Harshaw entered crystal growth in the 1930s with LiF crystals as a substitute for fused quartz with optical resonance at around 3 microns for analysis of compounds containing CH_2, i.e., organic compounds. LiF has excellent vacuum ultraviolet performance from 3 microns down to 1 micron. So, optical spectrometry using LiF revolutionized the analysis and synthesis of organic compounds. Pure sodium chloride (NaCl) was developed beginning in 1937 for similar applications. Harshaw grew synthetic sapphire and ruby from pressed Al_2O_3. Hot-pressed magnesium fluoride (MgF_2) is the infrared detector material used in heat-seeking missiles, smart weapons and some night-vision devices.



Dr. David Hammond

In the late 1940s, sodium iodide doped with thallium (NaI((Tl)) was found to produce scintillation from incident ionizing photon radiations and patented as a scintillation material by Robert Hofstadter and colleagues. Circa 1950, John Harshaw, son of the founder of the Harshaw Chemical Company, initiated interest in growing NaI(Tl) crystals by the Stockbarger method. Dr. Stockbarger, from MIT, was a consultant to Harshaw for optical crystal growth during previous years.

In 1952, Elmer Stewart, then the sales manager for the C&EP Department, unveiled two freshly canned NaI(Tl) crystals (½″ × ½″) at the second annual IEEE Nuclear Science Symposium to loud acclaim and great popularity. Sodium iodide doped with thallium was hygroscopic and need to be hermetically sealed or canned. Mr. Stewart later ascended to be the vice president and general manager of the department.

During the remainder of the 1950s, 1960s and even into the 1970s, Harshaw made dramatic improvements in terms of crystal growth including increasing crystal sizes, crystal quality and configurations for NaI(Tl) and other scintillation, optical and thermoluminescent crystals. For example, by 1970 Harshaw was able to grow NaI(Tl) crystal as large as 32″ diameter and 12″ thick.

One unique application for large NaI(Tl) crystals has been the configuration(s) termed "crystal ball." One such configuration constructed for the Stanford Linear Accelerator comprised several hundreds of NaI(Tl) pyramidal crystals in a spherical array approximately six feet in diameter with a photomultiplier tube mounted on each crystal. The crystal ball was then deployed in a collider beam in the accelerator looking at the interaction of high-energy nuclear particles and the resultant reaction.

NaI(Tl) is and has been widely used in imaging cameras for nuclear medicine applications. NaI(Tl) continues to be the most widely used scintillation crystal material in the world.

In the meantime, Harshaw also developed some other scintillation crystals to meet various customer needs and applications including CsI(Tl), CsI(Na), BaF_2, CaF_2, LiI, PbF, and a few others. The ^{6}LiI is used for neutron detection, the BaF_2 (pure) is an example of a high atomic number (Z) photon detector and PbF_2 is an excellent Cherenkov radiation detector. More recently Bismuth Germanate (BGO) has been developed for some applications. The positive properties of BGO include no need to be canned and it maintains its polish.

The story of LiF as a thermoluminescence (TL) radiation detector is a part of the lore of Harshaw and much of this legend has been published elsewhere. Please refer to Reference 2 in the attached bibliography. Circa 1950, Dr. Farrington Daniels at the University of Wisconsin viewed lithium fluoride (LiF) as an excellent candidate as a radiation dosimeter for civil defense applications. With the low atomic number (Z) of LiF, approximately that of air and soft human tissue, it seemed to be a nearly ideal detector material. At about that same time, Dr. Daniels contacted Harshaw for some samples of LiF to explore the radiation detection properties of that material. Lo and behold, Daniels found that LiF of that vintage first exposed to ionizing radiation and later heated produced thermoluminescence. Dr. Daniels published his results in the early 1950s showing that LiF had a measurable and linear TL response from about 10 rads up to about 500 rads. This qualified LiF as an excellent potential dosimetric material for civil defense purposes. The rad is defined as 100 ergs per gram of deposited radiation energy in any material.

In 1960, John Cameron at the University of Wisconsin wanted to continue the earlier work of Farrington Daniels for medical physics applications and again requested LiF samples from Harshaw. By that date, Harshaw had grown LiF crystals so pure that the contemporary LiF did NOT thermoluminesce. It took several years of cooperative effort between Harshaw and the University of Wisconsin to reproduce the LiF material of 1950 that did produce thermoluminescence. Dr. Swinehart published the US patent in 1967 for LiF as a TL material. This important reference is also included in the bibliography along with some of Dr. Swinehart's other accomplishments.

Thermoluminescence dosimeters (TLDs), along with complementary TL measuring instrumentation developed by Harshaw, have been used worldwide for some decades for photon, beta and neutron dosimetry.

SOME OF THE STORIES

Some of the following narrative is in chronological sequence, while some is more random in time. Products first produced by Harshaw and some others made possible by Harshaw-developed chemicals or methodology are underlined in the text.

In the 1890s, the Harshaw Chemical Company was founded as a partnership, Harshaw(WA)-Fuller-Goodman. This company manufactured some chemicals, resold some, and imported others. Among the more important products manufactured by Harshaw were hydrofluoric acid (HF), 30 to 60%, and ammonium bifluoride, NH_4HF_2. Both were used to etch glass. The hydrofluoric acid was made using stationary cast iron retorts from 1907 to 1919. In 1919, Charlie Park and William J. Harshaw (a son of the founder) developed a new rotary gas-fired retort, called a ball-mill operation. The starting material was crushed fluorspar or fluorite (CaF_2), obtained from gravel from iron and aluminum mining. The best of these mines were in southern Illinois and northern Kentucky. Flotation powder was just coming into the market in 1937, a byproduct of tailings from the mines. By adding 93% sulfuric acid (H_2SO_4) to the fluorspar in a lead tank, Harshaw was able to make hydrofluoric acid (HF) at concentrations of 60% and beyond.

Starting in 1937, Harshaw began a large-scale 24-hour HF retort with powdered spar and 101% sulfuric acid to produce *pure* and *anhydrous HF.* Anhydrous HF made possible both *synthetic rubber* and the *alkylation* of *aviation gasoline*.

Antinomy trifluoride (SbF_3), developed by Harshaw, was used to make *freon* (CF_3Cl). *Teflon* (C_2F_4), a widely used inert and high-temperature plastic, is calcined and polymerized freon.

In 1936, Harshaw developed boron trifluoride (BF_3). This chemical is used as a catalyst in the development of *synthetic butyl rubber,* giving us inflatable tires and that entire family of modern products. Until that time, we bought BF_3 from Germany. Today's high-temperature plastic electronic *circuit card substrates* are just one example of BF_3 in catalytic action.

In the late 1930s, Dr. Harold Booth at Western Reserve University interested Harshaw in lithium fluoride (LiF) as a substitute for quartz for better ultraviolet and infrared transmission. In about 1937, the Harshaw company (working in conjunction with Donald Stockbarger of MIT) developed seven-inch-thick LiF prisms that were used in infrared controls in oil refining. During that same period, Harshaw developed sodium chloride (NaCl), potassium bromide (KBr) and cesium bromide (CsBr), 60 mm × 60 mm prisms used in spectrometric analyses.

These optical prisms revolutionized the production of many organic materials. For example, Perkin-Elmer used the Harshaw prisms in controlling processes, such as the manufacture of DDT, polyethylene and many other organic compounds.

Also in the late 1930s, Harshaw developed crude oil-cracking catalysts, such as aluminum oxide (Al_2O_3), plus chromates and nickel as needed, breaking down oil into monomers such as the ethylenes and propylenes (and more).

In other words, Harshaw responded to the needs of other industries. The Harshaw chemistry research laboratories were at the leading edge in the development of catalysts, electroplating, ceramic colors, fluorides and inorganic salts and optical crystals. Harshaw also sold or re-sold pure, reagent grade chemicals such as sodium chloride. These innovations, developments and processes all contributed to the success of the company.

Moreover, Harshaw also developed silver chloride (AgCl) used by salt-water batteries, which are employed in torpedoes and sonar buoys to detect the presence and motion of submarines. Dr. H.C. Kremers realized that he needed help and experience in rolling "Clago" sheet, AgCl, for the Army Signal Corps. Through channels, Harshaw and the Signal Corps asked the steel company in Lorain, Ohio, for someone with experience in rolling steel that would roll the new material (AgCl).

The answer came down that Harshaw already had Ed Jablon working at Harshaw's Elyria plant. During World War II, Ed rolled AgCl at the East 97th Street (Cleveland) laboratory. In the 1950s, Ed also designed many of the crystal growth furnaces for NaI(Tl) producing crystals up to 19-inch diameters in Elyria and then 32-inch diameters in Solon. He had a technique for operating growth furnaces without leaving a trace of the positioning probe in the center of the crystal. Other operators left many small marks or voids in the center of crystals after touching the crystal with the position measuring probe.

Two days before the Japanese attack on Pearl Harbor—December 5 1941—Doctors Carl Swinehart and Harold Kremers of Harshaw accepted a firm order for 50 pounds of *uranium hexafluoride* (UF_6) at $50 per pound!! Until then, this extremely important compound was only made in small, laboratory quantities. Uranium hexafluoride was the raw material used to produce enriched ^{235}uranium by the gaseous diffusion process first used at Oak Ridge, Tennessee. Enriched uranium was and is still used throughout the nuclear weapons laboratories and nuclear power Industries, and gaseous diffusion remains the primary process for the enrichment of uranium.

The former headquarters of the Harshaw Chemical Company headquarters is now part of the Cleveland Clinic on East 97th Street, Cleveland, Ohio. The black stone construction is a unique architectural feature in this neighborhood in Cleveland. Photograph used courtesy of "The Nuclear Traveler."[1]

Now we briefly go back in time.

In the 1880s, French scientists produced fluorine gas—using fused potassium bifluoride (KHF_2) and graphite or platinum electrodes—only as a curiosity. A fluorine cell was demonstrated at the World's Fair in 1900 in Paris, France.

In 1937, Dr. Swinehart operated a small fluorine (F_2) cell at the Harvard-Dennison plant for Harshaw. Using a nickel anode, anhydrous hydrofluoric acid and potassium biflouride, Dr. Swinehart made fluorine (F_2). The process to make UF_6 generally goes like this, beginning with uranium oxide (UO_3):

$UO_3 + H_2 \rightarrow UO_2 + HF \rightarrow$

UF_4(green salt) + $F_2 \rightarrow UF_6$ (a gas).

Doctors Swinehart and H.C. Kremers made the UF_6 using the fluorine cells that each had developed independently at the East 97th Street (Cleveland) laboratory and he Harvard-Dennison plant respectively.

A group of experts met each month to discuss progress in design and operation of fluorine cells, and included representatives from DuPont, Hooker Chemical, Johns Hopkins University and Harshaw Chemical. Troubles with polarization were never the same for all. Harshaw was first to operate at 1000 Amps with more of these fluorine cells on individual generators. Area "C" at the Harvard-Dennison plant produced ALL of the feedstock for atomic energy and nuclear weapons until 1954.

Westinghouse also made the uranium tetrafluoride (UF_4) into a uranium metal called "tuballoy". Thanks to suggestions from Professors Brown and Fowler at Johns Hopkins University, Harshaw also used a tin reduction process to make sodium-uranium fluoride ($NaUF_5$) and, subsequently, uranium hexafluoride (UF_6). The demand for uranium metal then exceeded the demand for uranium hexafluoride, signaling the need to make ^{239}plutonium from uranium metal at the Hanford production reactors. As a note, calculations indicated that less ^{239}plutonium was needed than ^{235}uranium in nuclear weapons.

Harshaw also supplied material for making uranium metal on a production basis using UF_4 and magnesium (Mg) in the high temperature or "thermite" reaction. Other companies also made uranium metal using this technique.

When asked why UF_6 was being shipped to Oak Ridge, the truck driver brought back the secret, "to be fabricated into horses' heads and to be finally assembled in Washington."

Dr. Swinehart visited Oak Ridge in July 1945 for a month. There he described his experimental fluorine apparatus with the key people on staff. Oak Ridge had made uranium oxide (UO_2) and uranium tetrafluoride (UF_4) and were about to make uranium hexafluoride (UF_6). Swinehart also recalls the hustle and bustle at Oak Ridge as that small town was hastily developed into a city in 1942 as part of the super-secret "Manhattan Project". He also recalled interacting with Dr. Harold Urey who headed the Oak Ridge chemistry laboratory. Dr. Urey first purified and identified deuterium ($^2H_1$) or heavy hydrogen.

Harshaw produced the feedstock for the Oak Ridge processing facilities for 13 years (1948 to 1961) on a "letter of intent." This Harshaw technology was later transferred to the Fernald (Ohio) plant for UF_4 and to the Paducah (Kentucky) plant for UF_6.

Harshaw personnel also participated in hydrofluoric acid burn studies, fluoride toxicity and dental fluoride studies. In collaboration with the dental school at the University of Rochester, one part per million (1 ppm) was found to harden teeth. Harshaw flew fluosilicic acid to northern Canada and Key West in Florida for population testing.

Additionally, some 49 men had worked with fluorides and HF fumes under John Winger in the fluoride department for an average of 19 years. In 1937, these men were guinea pigs for a study by a group of doctors and dentists. Petroleum refining and other industries were planning changes that would expose many other men to fluoride. One group of dentists from the University of

Rochester, having shown that fluoride caused mottled teeth in children when second teeth were forming in the jaw, were interested in adult data. These 49 men at Harshaw had NO mottled teeth, and if anything, had fewer colds and cavities.

It is amazing to note that "mother nature"—via phosphate beds—holds seawater at about 1.4 parts per million of fluorine (F^-) ion. Also, CaF_2 is soluble to about 9 ppm and causes mottled teeth. Trees remove fluoride from groundwater when it is more than 1 ppm by precipitating $AlCO_3F$, thus preventing mottled teeth in those who eventually drink that groundwater. Coal ash is typically 60-90 ppm F because coal is compressed, petrified trees.

As mentioned earlier, the original Harshaw fluoride production plant started in 1907. The new plant started up in 1939, making pure anhydrous hydrofluoric acid used in making aviation (extremely high-octane) gasoline.

Some twelve or so employees of the new HF plant were needed to operate the plant and all were drafted into the US Army. Each passed the induction examination and each was honorably discharged *six hours later.* This underscores the importance of the Harshaw operation to produce UF_6 for use in the Manhattan Project.

SOME ADDITIONAL RELEVANT NOTES

The Harshaw Chemical Company was founded by William A. Harshaw, who had two sons, William J. and John Harshaw. A grandson, W.A. Harshaw, was also president of the company and promoted the Solid State Department at Prospect Avenue.

Harshaw was acquired by Kewaunee Oil Company in 1964. Kewaunee Oil was then acquired by the Gulf Oil Company in 1976. Kaiser Chemical Company next acquired the Harshaw interests in 1982. Engelhard Corporation acquired some of Harshaw in the late 1980s, and existing former Harshaw interests are currently under the management of Saint Gobain, a French consortium.

The Harvard-Dennison Harshaw plant contained "Plant C" which produced the uranium hexafluoride for the nuclear weapons/fuel programs. During World War II, Harshaw was mandated to recall all of the uranium-colored pottery, containing carnotite, a uranium ore, bright orange in color. This pottery is also termed "Fiestaware."

At one time, Harshaw had testing laboratories around the nation. The Boston testing laboratory developed nickel-plated holes for use in the gaseous diffusion process with uranium hexafluoride (UF_6). Nickel plating was a specialty with Harshaw.

Among the other people at Harshaw who distinguished themselves was Arthur "Mike" Michalske, who started as a compressed gas expert at Ohio Chemical. He developed methods of making ClF_3 and anhydrous HF into plant operations. He was also the plant manager at the Elyria facility that grew crystals. His foreman was Cliff Rowe.

John Winger worked in the fluoride department from 1907 into the 1950s, primarily as a foreman. He was a self-taught man, termed a skilled "lead-burner," sealing pipe joints. "Lead-burning" was considered a closed art, completely different from welding, and John Winger was considered the best under any conditions by those who worked for him. At one time lead-burning was done in a tent to avoid the spectators and the effects of wind. Lead was used to limit sulfuric acid and hydrofluoric acid to concentrations of about 60%. Stainless steel was/is needed for higher concentrations of hydrofluoric acid.

Another notable Harshaw product was tartaric acid, made from grape seeds and sulfuric acid. Tartaric acid is used in baking powders. Harshaw left this business in about 1939 because of poor yields.

Soon after the tartaric acid operation was shut down in Elyria, Ohio, the space and equipment were used to make cobalt carbonate. This was done on a temporary basis from a Cu-Fe-Co alloy from the Belgian Congo, rather than risk shipment directly to Belgium. During the war, copper and cobalt compounds were used. After the war, the accumulated iron cake was calcined for use in shoe polish. From 1954 to 1969, the plant space in Elyria was also used for optical and scintillation crystal production before the move to Solon, Ohio.

Harshaw was also a leader in the development of catalysts of various types. Mentioned earlier were those catalysts used to fractionally distill or "crack" oil into simpler organic compounds. Cobalt was used as a catalyst in linseed-oil-based paint dryers. Cobalt is also used in aluminum-nickel magnets for small DC motors and magnehelic-type gauges. Cobalt is also used in blue colors, and hardened stellite tools contain cobalt.

CONCLUSIONS

Many more short stories could be written about this diverse, innovative and creative company now relegated to history.

The Harshaw Chemical Company, its successors, and offspring, have contributed significantly to our society in countless peaceful applications and in defense of our nation. Some of the many excellent scientists, inventors, business managers and technical consultants are mentioned in this document along with some of their dedication and accomplishments. Those of us who worked for the Company are most proud to have been part of this quiet history of 100 plus years, and will always nostalgically remember the HARSHAW CHEMICAL COMPANY.

Morgan Cox
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The Patents of Dr. Carl Swinehart

Here are some of the more important patents authored or coauthored by Carl Swinehart:

- US Patent 2,118386, May 24, 1938: *Hydrofluoric Acid Composition* (Frosting mixture used in frosting glass).
- US Patent 2,196, 907, April 9, 1940: *Preparation of Compounds of Fluorine* (Included are the manufacture of BF_3 gas compressed in cylinders for use as a catalyst in making butyl rubber (inflatable) and as an amine complex for setting epoxy resin).
- US Patent 2,200,221, May 7, 1940: *Manufacture of Fluorescent Lamps.*
- US Patent 2,534,638, December 1950: *Electrolytic Production of Flourine*.
- US Patent 2,550,173, April 24, 1951: *Process for the Purification of* CaF_2 *and LiF for Manufacturing Macrocrystals*.
- US patent 3,167,391 January 26, 1951: *Purification of HF.*
- US Patent 3,320,180 May 16, 1967: *Thermoluminescent Doubly Doped LiF.*

There are many more similar patents by Dr Swinehart.

The commercial value of the many patents authored or coauthored by Carl Swinehart is in the billions of dollars in commercial sales.

References

1. *"The Nuclear Traveler*," website promoting the book, *The Travelers' Guide to Nuclear Weapons,* Timothy Karpin and James Maroncelli, authors. Published 2002, Historical Odysseys Press, Silverdale, Washington. Website accessed November 2003, www.atomictraveler.com .

2. Cox, M., Guest Editorial entitled "The Role of the Affiliates in the Health Physics Society," *Health Physics,* Volume 34 (May), pp 417-418 (1978).

About the Author

Mr. Cox is a Certified Health Physicist and a Fellow member of the Health Physics Society. He served for 18 plus years with the Crystal and Electronics Department of the Harshaw Chemical Company as product manager, sales manager and marketing manager for health physics products including the very successful TLD program. He worked closely with both Doctors Hammond and Swinehart during his tenure at Harshaw. He has also served in key management positions for Westinghouse Electric, Victoreen Instruments and Eberline Instruments. He is currently a senior consultant to the Department of Homeland Security (DHS), developing standards for the use of radiological instruments by DHS responders.

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