

WOMEN CHEMISTS IN THE NATIONAL INVENTORS' HALL OF FAME: THEIR REMARKABLE LIVES AND THEIR AWARD-WINNING RESEARCH

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The National Inventors' Hall of Fame (NIHF) celebrates the creative and entrepreneurial spirit of great inventors by showcasing exhibits and presentations that allow visitors to experience the excitement of discovery, creativity, and imagination. Founded in 1972 and located in Akron, Ohio, USA, the Hall of Fame is dedicated to the individuals who conceived the great technological advances which the USA fosters through its patent system. Each year a Selection Committee composed of representatives from national scientific and technical organizations votes to select the most qualified inventors from those nominated for the current year. To date, only 13 women of the more than 375 inventors thus honored are members of the Hall of Fame, and of these 13, six are chemists (1): Rachel Fuller, Brown, Gertrude Belle Elion, Edith Flanigen, Stephanie Louise Kwolek, Helen Murray Free, and Patsy O'Connell Sherman.

One may ask what circumstances gave rise to the induction of each of these women. Their successes spanned the entire 20th century; some were inducted at the height of their careers, and others were admitted to the NIHF posthumously. In examining their very diverse careers, each of them was characterized by several or all of the following qualities: drive to better the human condition, hard work and perseverance, systematic and consistent experimentation, collaborative efforts with one

other individual or with a team, taking advantage of a serendipitous event, curiosity, creativity, innovation, and a passion for chemistry. The qualities most applicable to each individual will be stressed in each section.

Collaborative Efforts, Financial Straits: Rachel Fuller Brown and Gertrude Elion

The lives and careers of two of the earliest inductees parallel one another in a remarkable way. Both Rachel Fuller Brown (1898-1980), inducted posthumously in 1994 (2), and Gertrude Belle Elion (1918-1999), inducted in 1991 (3), carried on their research in close collaboration with one other scientist.

Brown carried on a long-distance joint effort with Elizabeth Lee Hazen (1885-1975), a mycologist and bacteriologist who single-mindedly pursued a search for an antifungal antibiotic. Brown brought the chemical skills needed to identify, characterize, and purify the various substances produced by culturing bacteria found in the hundreds of soil samples they examined.

Prior to their work, there was no antifungal agent that matched the efficacy of penicillin and streptomycin against bacterial infections. Hazen felt that such an agent might be found by examining a wide variety of soil samples, since streptomycin had been found in the same

way. The samples she studied came from many sources worldwide. If a preliminary test showed antifungal activity, she sent the sample to Brown in order to extract the active component—by a painstaking series of solvent extractions since methods like HPLC were not available at that time. Fig. 1, taken from the original patent application (2), illustrates the multistep method needed prior to the advent of chromatographic methods.

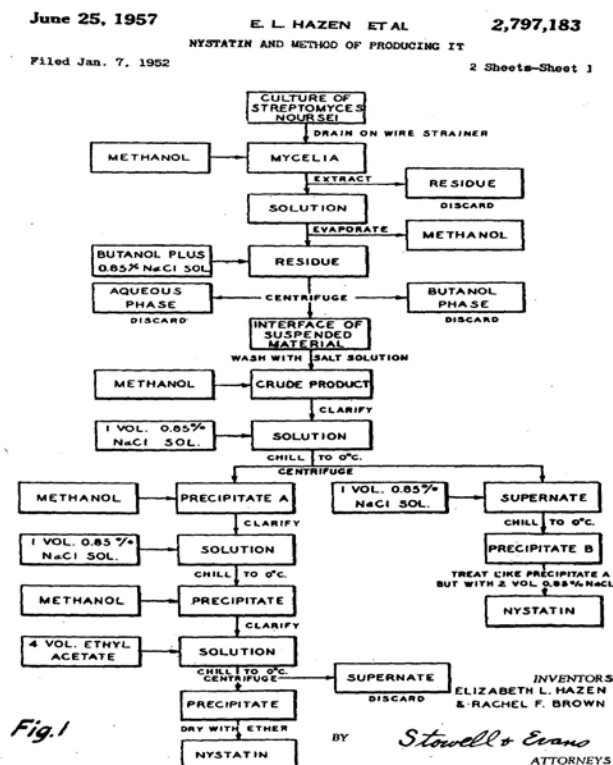


Figure 1. Brown's Scheme for Extraction of Nystatin A_1 from *Streptomyces noursei* Culture

Virtually all were found unsuitable for human use because the microorganism activity was too toxic. Hazen herself serendipitously discovered the winning candidate in a soil sample taken from a farm in Virginia where she was visiting her friends, the Nourses. She grew large quantities of this previously unknown organism (later named *Streptomyces noursei* in honor of its source), so that Brown could extract usable amounts of the active component. The antibiotic they developed, named 'Nystatin' for the New York State Department of Health, was first introduced in practical form in 1954 following Food and Drug Administration approval (4, 5). Further work revealed the presence of three biologically active components in the extract called, respectively, Nystatin

A_1 , Nystatin A_2 , and Nystatin A_3 . The structure (Fig. 2) of Nystatin A_1 was determined more than twenty years after its discovery (6).

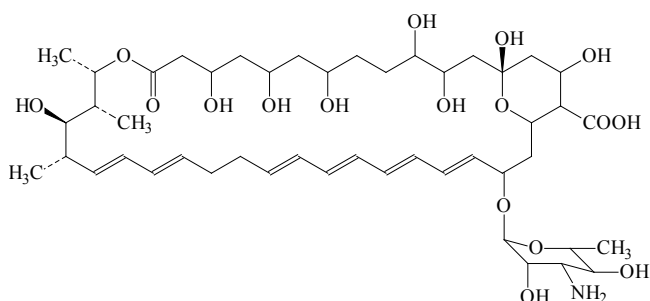


Figure 2. Nystatin A_1

Not only did Nystatin cure many disfiguring and disabling fungal infections of the skin, mouth, throat, and intestinal tract, but it could be combined with antibacterial drugs to balance their effects. Uses for Nystatin have been as varied as treating Dutch elm disease to rescuing water-damaged works of art from molds and mildew.

Gertrude Belle Elion's cooperation in drug development with a very unusual biochemist, George Hitchings (1905-1998), mirrored Rachel Fuller Brown's experience in many ways but diverged in others. Hitchings invited Elion into his Wellcome research laboratory (later Burroughs Wellcome) at a time when women found it difficult to secure scientific positions, and he continued to encourage her in her career development long after the hiring spurt for women during World War II was over (7). His was, at first, a helping role, whereas Brown and Hazen were equal copartners from the beginning. There were also differences and similarities in their scientific approach. Historically, drug developments frequently resulted from a trial-and-error process. As a consequence, the element of chance has been essential in developing new pharmaceuticals, as we have seen in the example of the suitable soil sample Elizabeth Lee Hazen found by chance. Gertrude Elion and George Hitchings, diverged from this traditional path in their research, using what is termed today "rational drug design." They methodically investigated areas in which they could see cellular and molecular targets for the development of useful drugs. During their long collaboration, Hitchings and Elion produced a number of effective drugs to treat a variety of illnesses, including leukemia, malaria, herpes, and gout.

The development of sulfa drugs by Gerhard Domagk (1895-1964) in the 1930s led the team to think that other substances that interfered with the metabolism of microbes—such as the sulfa drugs had been shown to

do—could also be developed as drugs. As a result, they began examining the nucleic acids, DNA and RNA, and their building blocks, the purines adenine and guanine. They soon discovered that bacterial cells cannot produce nucleic acids without the presence of certain purines. They then set to work on antimetabolite compounds, which locked up enzymes necessary for incorporating these purines into nucleic acids.

By 1950 this line of research had paid off. Using references from the old German literature, Elion and Hitchings synthesized two substances: diaminopurine and thioguanine, which the enzymes apparently latched onto instead of adenine and guanine. These new substances proved to be effective treatments for leukemia. Elion later substituted a sulfhydryl group ($-SH$) on a purine molecule, thereby creating 6-mercaptapurine (also known as 6-MP and trade named Purinethol); and subsequent substitution of a 2-amino group gave rise to the molecule which they patented and for which Elion was inducted into the Hall of Fame (8).

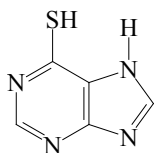


Figure 3. 6-Mercaptopurine

After this success they developed a number of additional drugs by using the same principle that had led them to 6-MP. Later these related drugs were found not only to interfere with the multiplication of white blood cells but also to suppress the immune system. This latter discovery led to a new drug, Imuran (azathioprine), and a new application, organ transplants. Imuran suppressed the immune system, which would otherwise reject newly transplanted organs (9).

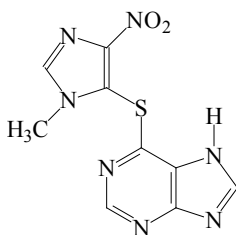


Figure 4. Imuran

Financial Difficulties and Altruism

Both Brown and Elion experienced great difficulty in financing their educations, and for both of them, their career trajectories were greatly impacted by these cir-

cumstances. For example, both financed their higher education by teaching high school, at least for a time. Brown's father deserted her family when she was just starting high school. A wealthy family friend financed her education at Mount Holyoke College where, as a history major, she took her first chemistry course to fulfill her science requirement. Hooked on chemistry from that moment, she continued as a double major, receiving her A.B. degree in 1920. She then went to the University of Chicago where she completed her Master's degree in organic chemistry, but then had to take time off to teach high school because of lack of funds. She was finally able to submit her Ph.D. thesis in 1926; but again, because of financial difficulties, she was forced to take a position with the New York State Department of Health in Albany, New York, and her thesis defense was thus delayed for another seven years. Brown, and Hazen, too, were especially fortunate to find a welcome in one of the few laboratories noted for hiring women, and also in receiving the help and encouragement from their laboratories administrator, Gilbert Dalldorf. It was he who promoted an announcement of the discovery of Nystatin in order to establish the Brown/Hazen priority.

Elion, born in New York City, attended the city's public schools, including Hunter College, where she received an excellent education although the crash of 1929, in which her father lost all his money, continued to shadow her for much of her early life. Elion lost her beloved grandfather to cancer while she was quite young, but this event was a major factor in her decision to study science so as to better the human condition. With her degree in chemistry (1937), she tried to enter graduate school but was rejected by 15 institutions. Instead she was offered a job washing dishes in a laboratory. She turned to teaching chemistry and physics in high school and meanwhile attended New York University on a part-time basis. Because of her financial hardship, she never completed her Ph.D. Nevertheless, she was hired by the Wellcome Research Laboratories, where she broadened her interests from chemistry to include biochemistry, pharmacology, immunology, and virology. She pursued her ground-breaking research at a time when there was virtually no scientific instrumentation, no carbon-14-labeled compounds to trace metabolites, and no theoretical basis since the Watson-Crick model of DNA structure had not yet been developed. Elion's work was recognized by the American Chemical Society in 1968 when she received the Garvan Medal, the Society's only award designated for women. Elion and George Hitchings shared the 1988 Nobel Prize in physiology or

medicine (10), along with Sir James W. Black (b. 1924). At the time of her retirement from Burroughs Wellcome, which had moved by this time to Chapel Hill, North Carolina, Elion became associated with Duke University as a research professor who mentored student research and taught pharmacology courses. Her academic life had come full circle.

Another remarkable parallel distinguishes these two women in the area of altruism. Brown (and Hazen) received no financial benefit from their work. They donated all Nystatin royalties—more than \$13 million by the time the patent expired—to academic science through the nonprofit Research Corporation. Furthermore, by the time of her death, Brown had repaid every grant-in-aid she had ever received in support of her education. Elion, in like manner, donated the fund she received from Burroughs Wellcome to match her Nobel Prize money to her Alma Mater, Hunter College, to further women's education in the sciences.

A Passion for Chemistry; Systematic and Consistent Experimentation; Effective Teamwork: Edith Flanigen and Stephanie Kwolek

Edith Flanigen (b. 1929) is one of the most inventive chemists of all time. Her creative and outstanding work in materials science and engineering has greatly affected modern life. Her discoveries have resulted in more than 100 patents and have revolutionized the world of molecular sieve materials. How did all this come about? In her own words, in an interview with the author, she said that you must love what you do because if there is any other reason for doing what you do, it just won't work. Edith's early inspiration came in high school where she and her two sisters were first introduced to chemistry. All of the Flanigen sisters were taught by Sister St. Mary, who emphasized hands-on activities and exciting demonstrations of chemical processes in her classes. After high school, first Joan, then Edith, and four years later Jane, as well, majored in chemistry at D'Youville College. There they took courses with Dorothea Fitzgerald, who was responsible for all chemistry courses. Both Joan and Edith earned master's degrees in chemistry from Syracuse University. All three Flanigen sisters eventually came to work at Union Carbide.

That early inspiration plus Flanigen's conviction that effective teamwork (within the same laboratory environment, as opposed to collaborative efforts separated by distance) and self-knowledge of one's own unique

characteristics and talents led to her playing a major role in the development of molecular sieve zeolites, a billion dollar industry that has impacted almost every area of life.

When Flanigen joined the Linde Division at Union Carbide in 1952, she was first assigned to silicone chemistry, and in 1956 she joined the molecular sieve group. Molecular sieves (or zeolites) are made of microporous materials that trap only molecules small enough to fit into their cavities while excluding larger molecules. This characteristic makes zeolites ideal for use as catalysts in various industrial processes.

It was primarily for this work that in 1992 she earned the first Perkin Medal ever awarded to a woman; the Perkin Medal is the highest honor for outstanding work in applied chemistry in the United States. She has received many other honors and awards during her 42-year career in industry, including the prestigious Lemelson-MIT Award in 2004 (11, 12).

While Edith Flanigen drew her early love of chemistry from her teachers, Stephanie Kwolek (b. 1923) attributes her love of science to her father. Kwolek's parents were immigrants from a town near Krakow, Poland. Both had the equivalent of a high school education and were voracious readers. Her father was an amateur naturalist, and Stephanie spent many hours with him exploring the woods and fields near home, looking at animals and bugs, as well as filling scrapbooks with leaves, wildflowers, seeds, grasses, and detailed descriptions. Her mother was primarily a homemaker (great cook, excellent seamstress, and terrific storyteller) who became a working parent after her husband's early death when her daughter was ten. In Stephanie's childhood she "played school" (of course, she was the teacher), drew hundreds of dresses and outfits (she considered becoming a fashion designer), wrote poetry and short stories (an early practice for her later chemical papers perhaps), but always returned to science.

Her elementary and high school education was a "mishmash" of public and parochial schools. She had no chemistry or physics courses in high school, only mathematics, biology and general science. When Kwolek graduated from high school, she entered Margaret Morrison Carnegie College of Carnegie-Mellon University and did a year of science courses (biology, chemistry, physics and mathematics, only 10-12 students per class) in addition to working 20 hours a week and making the honor roll (to her surprise). Kwolek was interested in medicine at the time. She majored in chemistry, minored

in biology and earned a B.S. degree in four years, working summer jobs and using various scholarships. As a high school sophomore, Kwolek was encouraged by a social science teacher and later two college chemistry professors were very supportive. After her college graduation, she was still interested in medicine but realized that expenses would be great. She decided to get a temporary job, save money, and enter medical school later. After interviewing at a number of companies, Kwolek decided that the work at DuPont was the most interesting and the starting salaries there were the same for women and men (not the case at other places).

Her interviewer at DuPont was Hale Charch, a research director at the company and the inventor of waterproof cellophane tape. Charch told Stephanie that he would let her know of his decision in a few weeks. Kwolek replied that she had other offers to consider and needed an answer sooner. Charch called in his secretary, dictated a letter making the job offer and gave it to Kwolek. She took the letter home, thought about it and accepted the offer. Reflecting on this bold request for a woman to make in 1946, Kwolek suspects that her assertiveness got her the job offer from DuPont. The polymer research she worked on was so interesting and challenging that she gave up the idea of medical school and made chemistry her lifelong career (13).

The chemistry accomplished by these two women is highly innovative and creative, born of team effort, and systematic, consistent experimentation.

Breakthroughs with Zeolites

Edith Flanigen's "claim" to the Hall of Fame in 1994 is for her contributions to the product development of Zeolite Y, an aluminosilicate "molecular sieve" used to make oil refining more efficient, cleaner, and safer (14). Flanigen began working on the emerging technology of molecular sieves, crystalline microporous structures with large internal void volumes and molecular sized pores, in 1956. These compounds can be used to purify and separate complex mixtures and catalyze or speed the rate of hydrocarbon reactions, and they have widespread application in the petroleum refining and petrochemical industries.

Natural zeolites occur in sedimentary and volcanic rocks, altered basalts, ores, and clay deposits. The 18th century Swedish mineralogist Axel Cronstedt coined the word "zeolite" from the Greek words "zein" (to

boil) and "lithos" (stone). He had observed that when a natural mineral was heated rapidly, the stones began to dance about as the water evaporated—they were literally "stones that boil." Chemically, natural zeolites are crystalline, hydrated alkali-aluminum silicates with mobile cations capable of undergoing ion exchange (15).

Since natural zeolite minerals are rare and difficult to obtain in large quantities, scientists developed methods of synthesizing zeolites in the laboratory as early as 1949. In the late 1970s, a team led by Flanigen was called upon by Union Carbide management to develop a new class of synthetic molecular sieves. By 1985 Flanigen and her team had filed more than 30 patents and had succeeded in developing a whole new generation of synthetic zeolites. Prior to Flanigen's work, it was thought that the electrovalent balance within the framework of silica and alumina tetrahedra during synthesis would be only attainable by having present in the reactant mixture a substantial quantity of metal cations, such as sodium. Once the metal cation had been included in the reactant mixture and the synthesis reaction completed, the metal ions that occupy the cationic sites of the crystal could then be replaced by a wide variety of other metallic cations using ion exchange techniques. Flanigen and her team succeeded in preparing for the first time crystalline zeolites containing a substantial weight percent of a cation other than sodium or other metal cation. This novel process afforded the incorporation of nonmetallic, nitrogenous cations, ammonium, tetramethylammonium ion, or lower derivatives such as $\text{NH}_2(\text{CH}_3)_2^+$.

These new zeolites were found to have a wide variety of applications such as separation of one fluid species from a stream containing many species by adsorption either preferentially or on the basis of the molecular dimensions of a particular fluid species. Unlike common adsorbents such as charcoal or silica gel which show selectivity based primarily on the boiling point or critical temperature of the adsorbate, the activated zeolites of Flanigen's invention exhibited a selectivity based on the size, shape, degree of unsaturation, polarity, or polarizability of the adsorbate molecule. Her patent application also noted that the rejection characteristics of the new zeolites were as important as the adsorption characteristics. The interstitial channels of these zeolites were such that at their narrowest points molecules with critical dimensions exceeding the pore diameter of the zeolite structure would not readily enter into the channels (Fig. 5).

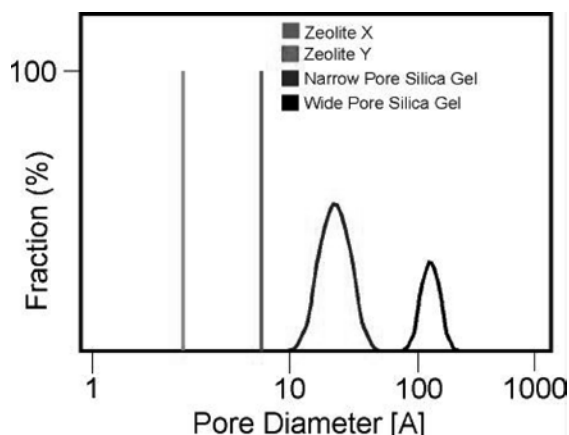


Figure 5. Distribution of pore sizes of zeolites and of silica gels

In addition, these zeolites were able to adsorb relatively large quantities of adsorbate at either very low adsorbate pressure or concentrations (Fig. 6), thus allowing these zeolites to be used to remove adsorbable impurities from gas and liquid mixtures, and also to recover minor components of such mixtures (14).

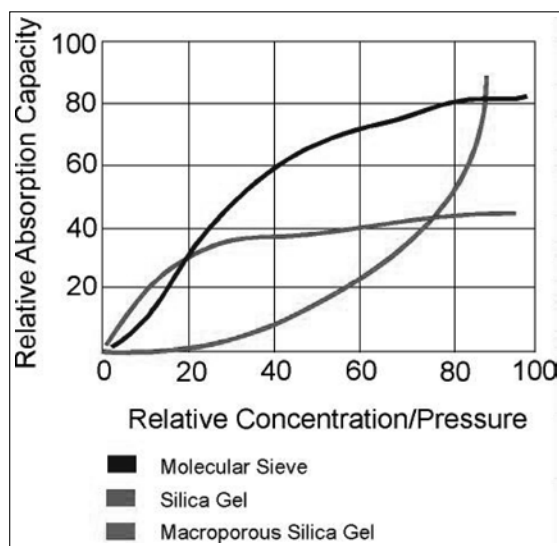


Figure 6. Relative adsorption capacities of molecular sieves compared with silica gels

When Jeffrey Seeman, in an interview with Edith Flanigen on April 6, 2008, asked her to what she attributed her breakthrough successes in novel zeolite development, she unhesitatingly replied that it was due to the unswerving dedication of a team of scientists whom she had personally selected for the work. She said that this teamwork made all the difference both in the quality and quantity of work achieved.

The First Synthetic Ultrahigh-Strength Fiber

All three of the characteristics highlighted in this section—effective teamwork, a passion for chemistry, and systematic creativity—enabled Stephanie Kwolek to make the breakthrough in the search for high-strength fibers. This search is very old, ever since sailors sought better cordage for their lines and sails, but right down to the 20th century, their choices were limited to natural fibers: hemp, manila, and cotton. Advances in this technology were only possible with the advent of synthetic polymers. Strong fibers depend upon the degree of alignment of the polymer chains, usually achieved by drawing out spun chains to fourfold their original length, a process that orients the polymer chains and markedly increases their strength. However, synthetic polymers, such as nylon, contain large portions of amorphous chain which are in random molecular order and contribute little to the fiber's strength (16).

In 1995 Stephanie Kwolek was inducted into the Hall of Fame for her discovery of an amazing group of super-strong polymers (17). Her earliest work pioneered low-temperature processes for the preparation of condensation polymers and resulted in hundreds of new polymers, including Kapton polyimide film and Nomex aramid polymer and fiber. As she carried out experiments to make stronger and stiffer fibers, she discovered an amazing branch of polymer science: liquid crystalline polymers of such great strength that the fruits of her inventiveness can be found in mooring ropes, fiber-optic cables, aircraft parts, canoes, and—most important to police—in lightweight bullet-resistant vests.

Kwolek, working at the DuPont Experimental Station in Wilmington, DE, made her breakthrough when she prepared a liquid-crystalline solution of poly (*p*-aminobenzamide) polymer that was spun to fibers with an extremely high tensile strength. These fibers could not be drawn because they were already fully aligned during the spinning operation. It was the liquid-crystalline nature of the spin solution that allowed for spontaneous alignment of the chains, thus overcoming the problem of amorphous chain parts that were strength-limiting. She selected as a monomer a *p*-aminobenzoyl halide salt represented in Fig. 7.

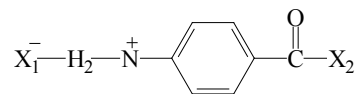


Figure 7. *p*-Aminobenzoyl Halide Salt Monomer

where X_1^- represents an arylsulfonate or similar group,

and X_2 represents a halide, preferably bromide or chloride. The resulting polymer had the formula shown in Fig. 8,

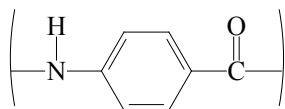


Figure 8. Homopolymeric Poly(*p*-Benzamide)

but it was insoluble in all solvents that had been tried up to this point (17). Kwolek needed to have the polymer in solution in order to spin it into fibers. She finally succeeded in dissolving it in tetramethylurea, producing an opalescent, turbid liquid crystal solution—a state of matter intermediate between truly liquid and truly crystalline. This was the first crystalline solution of an aromatic polyamide. Later it was shown that liquid-crystalline solutions are composed of small domains where polymer chains are perfectly aligned with respect to each other. Spinning these solutions causes enough shear to rotate the liquid-crystalline domains so that they align in unison, reaching a high state of orientation that is retained as the fibers coagulate (16). DuPont's development of this and other fibers that are up to five times stronger than steel led to such products as lightweight building materials, inflatable boats, airplane parts, ropes and cables, and bullet-proof vests (18).

And so, someone who did not have enough money to realize her dream of attending medical school went on to accomplish a larger dream evoked from centuries past: ultra-high strength synthetic fibers. She became so interested in this work that she remained at DuPont for her entire career, retiring in 1986. By her own admission, she was driven onward by her love of basic science and the fact that she was fascinated with the process of discovery. She has received many honors, including the Perkin Medal in 1997, the Kilby Award, the National Medal of Technology (1996), and the American Chemical Society Award for Creative Invention. Her name appears on 17 patents issued between 1961 and 1986 (19).

Innovation, Hard Work, and Perseverance: Helen Murray Free and Patsy Sherman

In 2000 Helen Murray Free (b. 1923) was inducted into the Hall of Fame for her contributions to the development of dry reagents that have become the standard in laboratory urinalysis and the more consumer-oriented “dip-and-read” tests, which first enabled diabetics to easily and accurately monitor and help control inde-

pendently their disease (20). Free's research in clinical chemistry not only revolutionized diagnostic testing in the laboratory but also in the home, where diabetics could test themselves. Free and her husband Alfred coauthored *Urodynamics: Concepts Relating to Urinalysis* in 1972 (21) and *Urinalysis in Clinical Laboratory Practice* in 1975 (22), which still remain standards in the field.

Helen Murray was born on February 20, 1923 to Daisy Piper and James Summerville Murray in Pittsburgh, Pennsylvania. In 1941 she graduated from Poland (Ohio) Seminary High School as valedictorian and then went on to the College of Wooster, where she graduated with a B.S. in chemistry in 1944. That same year she accepted a position as a control chemist at Miles, Inc. (which later became Bayer). She worked her way up the corporate ladder while developing and teaching both management and technical courses. She retired in 2007 as Professional Relations Consultant in the Diabetes Care Division. Free has also been awarded seven patents for her clinical diagnostic test inventions.

Early on at Miles, Helen collaborated with biochemist Alfred Free. Helen married Alfred Free in 1947 and they had six children. He died in 2000 (23, 24).

The Free invention had as one of its primary objects the provision of a simple, rapid, and convenient means for performing a test for the detection of glucose with a high degree of simplicity and without the need for extensive equipment or trained personnel. There have been available over the years a number of methods to measure the amount of glucose in urine. The more widely used of the conventional methods are based on the use of alkaline copper solutions which are heated with the materials being tested to precipitate copper (I) oxide (Fehling's Test; Benedict's Test). The disadvantage of these methods is that their use has required a certain amount of skill and familiarity with the use of measuring equipment such as pipets and graduated cylinders, and the use of liquid reagents some of which were dangerous to handle and inconvenient to transport. Furthermore, these tests all required heat supplied by an extraneous source, such as a Bunsen burner. On the contrary, the Free invention was a highly effective means for detecting glucose in various materials that is specific, economical, rapid, convenient, reliable, does not require use of any heat source, and lends itself to mass screening of people for diabetes detection.

The invention consists of two enzymes, glucose oxidase and peroxidase, an indicator whose color is affected by hydrogen peroxide in the presence of one of

these enzymes, and a buffer to maintain the pH within a predetermined range, a stabilizer such as gelatin, and in some cases a dye to make color reading easier. The reactions are as follows (20).

Glucose oxidase + Glucose + O₂ (atmospheric) → Gluconic acid + H₂O₂

H₂O₂ + Peroxidase + Dye (Reduced form) → Dye (Oxidized form) [Color change]

Free likes to tell the story about another of her inventions, a urine protein test using the dipstick method, which she helped popularize while working in the Technical Services Department, where she fielded questions from customers. Many of these customers were medical technicians who did not take kindly to her trying to make testing for them more convenient. They felt that if anybody could do dipsticks, the technicians would lose their jobs to, as they put it, to “kids off the street.” The protein test was based on the protein error of certain pH indicators, and the color change was from yellow to blue (beginning with pH 4). When one medical technician complained that she never got a negative answer with these new-fangled reagents, Helen asked if she followed directions and dipped the strip quickly into the urine specimen. She replied, “Oh, no, of course not. I stir it around to get the last little bit of protein out” And so she was actually washing the pH 2 buffer off the strip—and every urine specimen has a pH of more than 4!!

Because of the tremendous impact of her work, Free has been awarded many honors, including the American Chemical Society Garvan Medal (1970), The Honor Scroll Award of the Chicago chapter of the American Institute of Chemists (1967), and the Kilby Foundation Award (1996).

Throughout her career Helen Murray Free has been an active advocate of science education. From 1987 to 1992 she chaired the ACS National Chemistry Week Task Force. In 1993 she was elected president of the ACS. Because of her extraordinary work in public science education, the ACS instituted the Helen M. Free Award in Public Outreach in 1995. She was the first recipient.

In a recent conversation with the author, Helen Free expressed some characteristics that she felt helped her enormously in her career both at home and at work. She said that innovation, hard work, and perseverance could only be sustained by flexibility, openness to opportunity, and a large dose of joy.

Serendipity, Creativity, Curiosity,

In 2001 Patsy Sherman (1930 – 2008) was inducted into the Hall of Fame for her creation of Scotchgard™ while working at the 3M Company. In the late 1960s her research culminated in the development of a product that both repelled stains and also permitted the removal of oily soils from synthetic fabrics, including the newly popular permanent press fabrics (25).

In 1952 fluoro-chemicals were not well understood. Chemist Sherman and colleague Sam Smith, working at 3M Company, were eager to find applications for them. Their most famous application, Scotchgard™, is one of the most widely used and valuable products, eventually bringing in over \$300 million annually for 3M. Their discovery of Scotchgard was serendipitous. After an accidental spill of a fluorochemical-latex emulsion rubber intended for jet fuel hoses showed resistance to water and oily liquids, they suddenly understood the potential of this mixture for the protection of fabrics. After much experimentation and testing, they patented Scotchgard and over a dozen other inventions.

Patsy Sherman was born in Minneapolis, Minnesota in 1930. She majored in chemistry and mathematics at Gustavus Adolphus College, receiving her baccalaureate degree in 1952. She then joined 3M as a research chemist and was assigned to work on fluorochemical polymers. Sherman was one of very few women chemists to work for a major corporation in 1952. Her work was an essential part of the introduction of 3M's first stain repellent and soil release textile treatments which have grown into an entire family of products known as Scotchgard® protectors.

Patsy Sherman regards the discovery of Scotchgard as one of her most significant accomplishments because many experts had written that such a product was “thermodynamically impossible.” She said, “We were trying to develop a new kind of rubber for jet aircraft fuel lines, when one of the lab assistants accidentally dropped a glass bottle that contained a batch of synthetic latex I had made. Some of the latex mixture splashed on the assistant's canvas tennis shoes and the result was remarkable.”

That day in the lab is legendary. Sherman and her colleague, Sam Smith, were working on another project when they observed that the accidental spill on a white tennis shoe would not wash off nor would solvent remove it. The area resisted soiling. They recognized the

commercial potential of its application to fabrics during manufacture and by the consumer at home.

As described in their initial patent application, their invention involves the synthesis of hybrid polymers that provide sufficient oleophobicity and hydrophilicity in water so that fabrics treated with the polymer have increased ability to release oily stains on laundering. They combined oleophobic and hydrophilic moieties in coatable copolymers, so that the relative mobility of the moieties was assured at normal conditions of temperature and environment. The surfaces treated with these copolymers responded reversibly to changes of environment, thus making them repeatedly launderable to remove oily stains.

An important characteristic of the hydrophilic segments of the polymer was that they be solvatable, and thus must contain structural units containing characteristic polar groups. One particular type of hydrophilic segment they used consisted of the product between hydrogen sulfide reacted and polyethylene glycol dimethacrylates to give sulfhydryl terminated prepolymers of the type called "H" to indicate hydrophilic:

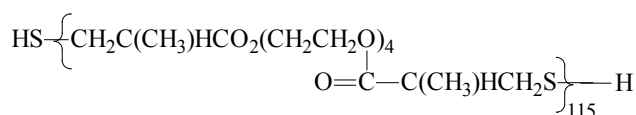


Figure 9. A Type "H" Prepolymer

A block copolymer is formed when an ethylenically unsaturated fluorinated monomer, called a Type "F" (to indicate "perfluorinated/oleophobic") monomer (Fig. 10) is polymerized by free radical initiation in the presence of the sulfhydryl terminated prepolymer. The segmentation of the polymer arises as a result of free radical chain transfer of the growing fluorinated polymeric unit to the sulfhydryl end groups.

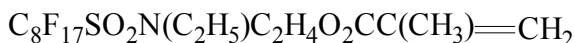


Figure 10. A Type "F" Monomer

Coating a surface with this polymer works in the following way. Fig. 12a shows diagrammatically an exposed surface treated with an oil and water repellent finish. The circles 10 designate the fluorochemical terminating groups which are seen when the surface is sufficiently enlarged. The terminating groups tend to be in some degree organized and will cover most of the

surface to form domains of oleophobicity. The ultimate end of each terminating group may be considered to be a trifluoromethyl group; the last three carbon atoms of a terminating group should be completely fluorinated to assure suitable oleophobicity.

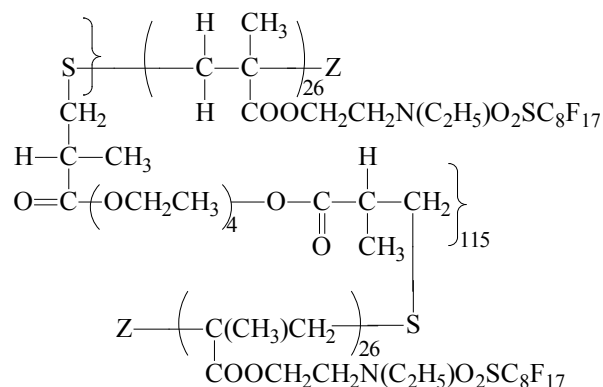


Figure 11. A Block Copolymer of the Type "F-H-F"

Fig. 12b shows an exposed hydrophilic surface comprised of hydrophilic constituent groups such as $-\text{COOH}$ and $-\text{OH}$. A fabric provided with such a surface is water-wettable and is cleanable by laundering. Prior to the Sherman invention it had been inconceivable that a given fabric could be treated so as to possess characteristics of both Fig. 12a and 12b depending on the environment and that change of environment would effect repeated reversal of the characteristics.

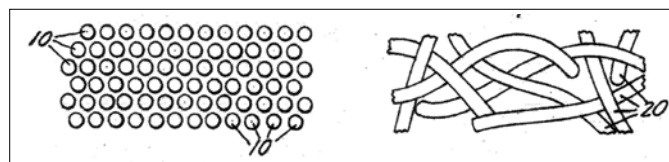


Figure 12a. Exposed Treated Surface Figure 12b. Exposed Hydrophilic Surface

Fig. 13 shows in highly diagrammatic fashion and in section, the outer layer of fiber 30 in a nonpolar, i.e., nonaqueous, medium such as air. Deposited on this surface is an autoadaptable segmented polymer having hydrophilic "H" segments designated by the strands 32 and hydrophobic and oleophobic "F" segments 36, 37, and 38, comprising a multiplicity of fluoroaliphatic or pendent groups, represented by slender rectangles 39, having fluorochemical terminating groups.

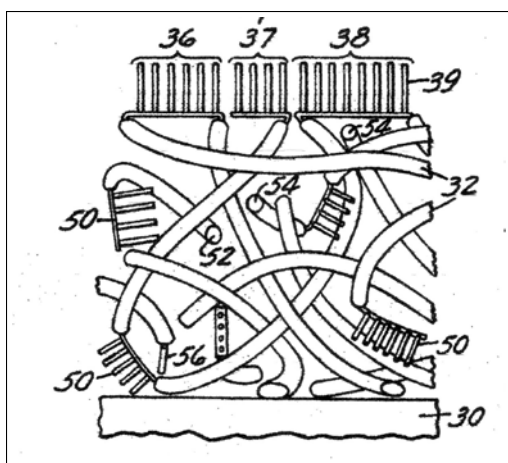


Figure 13. Fiber surface upon which is deposited an “F-H-F” segmented polymer

Fibers treated with an “F-H-F” segmented polymer can be cleansed in a mode that is quite different from normal cleansing action by emulsification. Soaps and detergents emulsify soil, which is normally hydrophobic and therefore can be dissolved in the hydrophobic portion of the soap or detergent, and then be dissolved in aqueous medium by means of the hydrophilic portion of the emulsion. On the contrary, cleansing action for an “F-H-F” treated fiber follows the sequence illustrated in Fig. 14:

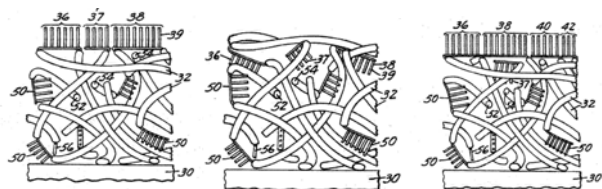


Figure 14a **Figure 14b** **Figure 14c**
Figure 14. Surface transformations of a type “F-H-F” polymer with changing environment.

In Fig. 14a the top of the fiber coating has an organized layer of oleophobic polymer which, when immersed in water (Fig. 14b) becomes submerged in the body of the polymer while the hydrophilic strands rise to the top. When the aqueous medium is removed, by drying, for example, a new surface of oleophobic polymer rises to the surface (Fig. 14c). Such movement repels oily stains and at the same time allows them to be washed away since they cannot adhere in any way to the fiber. The coating is self-renewing, thus allowing for multiple washings of the coated fiber.

After the introduction in 1956 of a stain repellent treatment for wool, Sherman and Smith later developed products designed for clothing, household linens, uphol-

stery, and carpeting. They jointly hold 13 patents in fluorochemical polymers and polymerization processes.

So an initial serendipitous event turned into a blockbuster invention through the follow-up curiosity and creativity necessary for the perfection of any invention. An interview with Sherman’s daughter, Shari Loushin (also a 3M chemist), revealed some of the qualities that helped her to follow the path of invention: high energy, competitive, active, feisty in the face of prejudice, and loyal to her profession and to the professionals with whom she worked. These characteristics enabled Sherman to continue to develop a whole new line of products based upon her initial discovery and eventually to move into a top managerial position at 3M.

Conclusion

In 1777, Restif de la Bretonne could write to his contemporaries: “All women should be prohibited from learning to write and even read. This would preserve them from loose thoughts, confining them to useful tasks about the house, instilling in them respect for the first sex.” (26). We have seen in this paper that “loose thoughts” arising from literacy, and not only from literacy, but scientific literacy, have given rise to useful inventions that have improved the quality of life of entire generations. Usefulness “about the house” has been transformed into universal usefulness, instilling in us all a respect for the female gender, not as a first, but as an equal participant in the field of human endeavor.

There are so many different characteristics that come into play in the field of scientific discovery. Many of these were touched on in the various sections of this essay. Each of the inventors highlighted here has attributed her success to several of these qualities, and while they might be necessary, one could never say that they are sufficient. The congeries of “success recipes” would never have worked unless each of these dedicated women, in her own way, were on a single-minded but multi-faceted trajectory that included as much emotional power as intellectual achievement, driven overall by a supreme sense of purpose. But in the end, is all analysis fruitless? Can outstanding success be diagrammed like a sentence or chromatographed for an ingredient profile? That barriers to success exist is evident. That these barriers can be overcome in a variety of ways that span every aspect of human endeavor is also clear, perhaps rendered even more so by the stories presented in this paper. But in the end, it all seems to depend on the indomitability of the human spirit, “free at last!”

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