

Agricultural and Food Chemicals

These compounds nurture the foundation of civilization.

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Agriculture and chemistry have a symbiotic relationship—manufactured chemicals are intrinsic to the growth and health of today's highly managed agricultural systems (fertilizers and pesticides), and in turn, agriculture provides the source of chemicals used not only in food production (additives and flavors), but also in a wide variety of industrial processes (chemical feedstocks, pulp, and paper). To fully understand this vast market, one must look at both sides of the relationship.

Down on the Farm

Sodium nitrate was the first commercial nitrogen fertilizer, mined from natural deposits in Chile and exported to Europe and North America from the 1830s. But in 1928, the United States started to produce its own synthetic version. The use of ammonium sulfate, which was a by-product of nitrate production from coke oven gases, made it the most important source of nitrogen for agriculture from the 1920s until 1944, when it, in turn, was surpassed by ammonium nitrate. Ammonium nitrate was then replaced by anhydrous ammonia and urea, which have been the main sources of nitrogenous fertilizer in modern industrial agriculture.

Although the first commercial ammonia synthesis plant opened in Germany in 1911 using the Haber-Bosch process, it was not until World War II that a significant increase in production and use occurred. By the 1960s, the M. W. Kellogg Co. developed the centrifugal compressor ammonia plant, which produced ammonia efficiently and in sufficiently large quantities that it accounted for more than one-third of nitrogen fertilizer use by the 1990s.

Phosphate fertilizer production was a different story because of the high availability of phosphate rock (which remains today the only economical source of phosphorus for fertilizer production). Phosphoric acid, used as a fertilizer, is obtained by treating the rock with sulfuric acid. In the United States, phosphate mining began in the mid-19th century and continues today. For example, promp-

ted by high returns in the phosphate fertilizer industry, in 1985 the Cargill Company acquired 80% of Gardinier, a Florida phosphate-fertilizer mining and manufacturing company.

In addition to fertilizers, a host of arsenicals, copper compounds, minerals, metals, and toxic oils—used to control insect infestations—was available to farmers beginning in the mid-19th century. For example, the Grasselli Chemical Co.

began manufacturing lime-sulfur insecticides in 1902 and lead arsenates in 1907.

Hydrocyanic acid gas fumigation methods were developed for control of insects affecting greenhouse plants by 1917. In 1918, a plane was first used for spraying insecticides, and improvements in planes and sprayers throughout the 1920s led to routine commercial use of planes for pesticide application.

By 1922, nicotine sprays, rotenone, and calcium cyanide dust were all available as insecticides for farm use. By 1926, DuPont had begun an insecticide research program, and it acquired Grasselli Chemical in 1928. In 1932, the Stepan Co. was founded as a distributor of calcium chloride, but it would evolve to produce calcium dodecylbenzene sulfonate as well—a surfactant used for even application of pesticides. Such surfactants are critically important agricultural chemicals, enhancing the value of insecticides and herbicides by enabling them to be efficiently sprayed in liquid form by truck or plane.

In 1939, Swiss chemist Paul Müller discovered the insecticidal properties of the first synthetic organic pesticide—dichlorodiphenyltrichloroethane, or DDT (an organochloride).

Similarly, scientists in Germany looking for new nerve gas agents during World War II synthesized the organophosphate insecticide parathion, which was first marketed in 1943 and remains widely used today.



Top: Herbicide spraying, Pittsburgh Coke & Chemical Co. ad, 1950, *Chemical & Engineering News*

Center: Nitric acid tanks, Chicago Bridge & Iron Co. ad, 1950, *Chemical & Engineering News*



AGRICULTURAL AND FOOD CHEMICALS



BIOTECH ROUNDUP

The main impetus to the growth of commercial agricultural biotechnology came from the demand for pesticides. And one of the most important of those was the herbicide Roundup (glyphosate), a Monsanto product first developed in 1970. Roundup became available as a postemergence, nonselective herbicide in 1974, as a result of the work of John Franz and colleagues. Because glyphosate is an indiscriminate plant killer, it could not be applied during the growth cycle of a crop, allowing weeds to flourish from sprout to harvest. If crops could be made resistant to Roundup, season-long weed control would be possible. This and similar herbicides—such as Liberty (glufosinate), a product of Bayer CropScience—led to corporate interest in the production of herbicide-resistant crops through genetic engineering, a situation that helped turn agricultural chemical companies into plant biotechnology institutes. By the end of the 20th century, pest- and pesticide-resistant biotech crops developed by the large agrochemical companies had transformed world agriculture. The U.S. Department of Agriculture estimated that 86% of the soybean acreage in the United States in 2004 will be planted with herbicide-resistant varieties (including Roundup Ready and Liberty Link varieties), although movement into other crop species, such as Roundup Ready wheat, is currently at a standstill.

Also as a result of World War II research, insect repellents such as dimethyl phthalate, benzyl benzoate, benzene hexachloride, and lindane were developed. In 1943, DDT began to be used for control of typhus and other insect-borne diseases, and by 1944, DuPont was manufacturing DDT on a commercial scale. Cyclodienes, including chlordane (1945); aldrin and dieldrin (1948); heptachlor (1949), which was first produced commercially by Velsicol Corp.; and endrin (1951) appeared after World War II.

Toxaphene is a mixture of chlorinated camphenes produced from pine resins containing more than 670 different compounds. It was developed in 1947 and had perhaps the most widespread use of any single insecticide in agriculture—although mostly in combination with stronger compounds such as DDT or parathion. Toxaphene works through disrupting insect

neurons, creating an imbalance in sodium and potassium ions. Its registration for most uses was banned by the U.S. Environmental Protection Agency (EPA) in 1982 and for all uses in 1990. The first-generation synthetic pyrethrum (or pyrethroid) was allethrin (Pynamin), which was developed in 1949. Its synthesis required 22 separate reactions to develop the final compound.

In 1951, the Geigy Chemical Co. in Switzerland introduced the first of the carbamates—a new class of pesticides that act similarly to organophosphates by inhibiting cholinesterase in insects. The first commercially successful carbamate insecticide, carbaryl (Sevin), was introduced in 1956.

Rachel Carson, in her book *Silent Spring* (1962), was one of the first to bring to the attention of the general public the long-term environmental effects of chlorinated pesticides such as DDT. As the result of the DDT controversy, the compound was banned in the United States in 1972.

New classes of insecticides are still being developed. The nicotinoids, for example, are modeled after natural nicotine—a time-honored pesticide. The first, imidacloprid, was introduced in Europe and Japan in 1990 and registered in the United States in 1992. It is marketed under several different trade names worldwide—including Admire, Confidor, Gau-

cho, Merit, and Provado—and has rapidly reached one of the highest-volume uses globally of all insecticides.

According to EPA, herbicides account for almost half of the aggregate value of world pesticides. One of the first important breakthroughs in this area came in the mid-1940s, when 2,4-D began being marketed as a selective, limited systemic herbicide. Throughout the 1950s and 1960s, herbicides grew into a major industrial concern.

For example, Monsanto's herbicide work began in 1952. From 1960 to 1972, Monsanto examined more than 51,000 compounds for herbicidal activity. Of those, 50 made it to the product development stage, with only 3 becoming commercial products, one of which was glyphosate (see sidebar).

Almost all of the leading chemical companies have been involved in the production of agricultural chemicals from their beginnings and retain a strong presence in the manufacture of these products and their intermediates, especially pesticides. These include BASF, Dow, DuPont, Eastman, FMC Corp., and Mitsubishi. Syngenta (formed in 2000 when Novartis agribusiness and Zeneca agrochemicals merged) and Bayer CropScience (a part of the Bayer Group formed when Bayer Crop Protection acquired Aventis CropScience) have the number one and two position, respectively, in the crop-protection industry.

Today, in addition to the bulk agrochemical producers, there are a variety of companies such as Bayer Chemicals and Isochem that provide important support for the development of new plant protection compounds, providing technical expertise in chemical processes such as phosgenation, nitration, hydrogenation, and multistage synthesis.

Equally, the need for appropriate dispersal technologies and chemistries remains, with smaller companies such as ISP and Stepan, and industrial giants such as Dow Corning providing a wide variety of means of dispersion, including emulsifiable concentrates, water-dispersible granules, microemulsions, microencapsulations, gels, flowable/suspension concentrates, and wetttable powders.

Shelved in the Market

Purified and semipurified agricultural components are at the heart of the food-processing industry. According to the Food Additives and Ingredients Association of the United Kingdom, the major categories of food additives are preservatives (such as propionic, sorbic, and benzoic acid and calcium propionate and potassium sorbate); antioxidants (such as citric acid, phosphoric acid, and ascorbic acid); gelling, thickening, and stabilizing agents; emulsifiers; colors; sweeteners; and acids.

Companies such as Nutrinova (formed in 1997 from Hoechst AG) and GPC produce a wide variety of food ingredients for the food and beverage industry. One particularly important food product from corn wet milling with a long history as a

Above: Sweet corn, Photodisc



Above: Saccharin, from the Monsanto Co., *Chemical & Engineering News*

source of food additives and chemical feedstock is corn syrup. Corn syrup technology has transformed the beverage industry, among others. In the mid-1950s, the technology for commercially preparing large amounts of maltodextrin and dextrose became available, leading to the ability of corn-based sweeteners to compete in some markets previously dominated by the sugar industry.

With the development of enzyme-catalyzed isomerization of dextrose to fructose, the production of high-fructose corn syrup (HFCS) became possible, the first commercial shipment occurring in 1967. With further improvements, by the mid-1980s, HFCS became the dominant sweetener in beverages and an intense competitor with sugar in nearly all areas of food sweetening. A host of companies supply the phenomenal demand for corn syrup products. For example, Roquette America (formerly the Hubinger Co., founded in the 1880s) produces commodities such as HFCS, dextrose, maltodextrins, and native and modified cornstarch products, as well as liquid and crystalline polyols for food and industrial use. Corn also serves as a significant fermentation source for many other important food compounds, including flavorings, for example, monosodium glutamate, which is produced by companies such as Ajinomoto.

Up to the Factory

The use of agricultural products for industrial purposes is not all that modern. Archer Daniels Midland (ADM) began in Minneapolis in 1902 as the Daniels Linseed Co., and in 1903 produced its first bottle of linseed oil. In 1934, ADM installed the first continuous solvent extraction system in the United States. In 1939, the company built the biggest vegetable oil processing plant, and throughout the 1940s, ADM used raw linseed and crude soybean oil to produce hundreds of different products for food and industry. Similarly, in 1943, Cargill (founded in 1890) entered the soybean-processing business with the acquisition of plants throughout the central United States.

Other companies showed similar trajectories. In 1943, for example, Gage Kent joined forces with S. G. Stein, a prominent Muscatine, IA, businessman, to found Grain Processing Corp. (GPC). The new company built a corn-processing plant to produce industrial alcohol for the manufacture of synthetic rubber needed in the war effort. When the war ended, the plant continued to operate, producing industrial and beverage alcohol, starch, and maltodextrins.

The production of ethanol by corn refiners began after World War II, but major quantities were not manufactured until the 1970s, when the mills began fermenting the now readily available dextrose to make beverage and industrial alcohol. Prompted by the 1978 Arab oil embargo, ADM, at the request of President Jimmy Carter, converted a new beverage alcohol plant to the production of synfuels.

Currently, although the wet-milling industry continues to produce its core products—starch, glucose, and dextrose—microbial fermentation products such as fructose and ethanol, and other chemicals, are becoming much more valuable for a wide variety of industrial applications. These include alcohols for fuel as well as chemical feedstocks for the production of adhesives, surfactants, inks, paints and coatings, soaps and detergents, cosmetics and toiletries, lubricants, plastics, and rubber.

Organic acids for industrial and food use are becoming ever more valuable. Starch, from corn or potatoes, purified or modified, for example, is routinely used in adhesives and as a filler for pharmaceuticals. And vegetable oils from several different plant species, including canola, soy, and flax, are routinely used as lubricants and feedstocks.

Other bioindustrial products are the product of sugar fermentation. The PURAC company, for example, beginning with lactic acid production in 1935, has become one of the world's largest manufacturers of natural lactic acid, lactates, and gluconates in factories in North and South America and Europe. Corn and other plant-crop-derived dextrose can be used to make polylactide polymers for fibers, plastic packaging, and other products, prompting increased production at the end of the 20th century by companies such as PURAC and Cargill Dow Polymers.

Similarly, the Omega Protein Corp. (originating from a fish-processing operation founded in 1878 by John A. Haynie and his brother Thomas, which became Haynie Products in 1968) derives products from menhaden, an omega-3-rich fish unsuited to modern seafood tastes. Fish meal protein and oils are used for industrial applications such as tanning, fatty acid production, and the production of alkyds for paints and coatings. Similarly, Cognis Oleochemicals (carved out in 1999 as a sector of Henkel KGaA) came to manufacture products from natural oils and fats, processing nearly a million metric tons of oils and fats yearly—derived mainly from coconut, palm, rapeseed, soybeans, and sunflowers.

Traditional agriculture-related companies such as Morton Salt also applied their previous expertise to the production of industrial chemicals. After becoming a major supplier of inorganics derived from salt, Morton created a division to produce organic chemicals, polymers, and agricultural chemicals. In 1999, Morton became a part of the Rohm and Haas Co.

Today, the use of foodstuffs as industrial feedstocks has become a priority in both Europe and the United States. With the growing demand for petroleum substitutes, and a burgeoning world population, many futurists believe the competition for agricultural production between the chemical feedstock industry and human consumption will be severe. Dealing with this issue may be one of the most significant creative challenges facing future chemists. ♦