

**The Rise of Chemical Industry in the United States due to World War I.
DuPont in the Nation's Service**

DuPont Corporation, a large American chemical and biotechnology company, is a major contributor to many industries ranging from construction, materials, electronics and agriculture. DuPont was established in 1802 as a manufacturer of gunpowder; however, in 1915 it began to shift its emphasis from gunpowder to the broad field of materials. This shift was a consequence of demands arising from resource shortages during the First World War. Because imports of chemical products from Germany ceased in 1915, DuPont initiated a synthetic-organic chemical industry in the United States. DuPont's need-driven decision to manufacture synthetic dyes eventually changed DuPont from a manufacturer of smokeless powder and other explosives to a diversified chemical-products company. The demand for a domestic dyestuffs industry required new expertise in organic-synthetic chemistry; while initially DuPont struggled with the task, in time, and with collaboration from both British and German experts, an organic-chemical industry in the U.S. was born, initiated by World War I.

Motivation for a Domestic Dye Industry

Prior to World War I, the US was dependent on Germany for imports of dyes and other organic chemicals. Germany dominated the synthetic-dye market with six major dye firms: B.A.S.F., Hoechst, Bayer, Cassella, Agfa, and Kalle (15, p. 262); these companies were responsible for 75% of the world's supply of dyes and nearly all dye

intermediates. As early as 1870, the German companies established distribution centers in the United States to sell their dyes (15, p. 261).

In 1883, the U.S. congress lowered the tariff on dyestuffs to 10% below the average American tariff level. The reduced tariff levels continued under the Tariff Act of 1913. Therefore, there was little economic incentive for the U.S. to develop a domestic industry (15, p. 263). The nascent, independent dyestuff industry in the U.S. could not compete with the already well-established German industry. The United States establishments making coal-tar products were assembling plants dependent on imported intermediates. In 1914, in the United States, the production of coal-tar dyes from such assembly plants (dependent on German imports) totaled 6,620,000 lbs valued at \$2,470,000 (16, p. 1). By 1917 the domestic industry in the US was producing 45,980,000 lbs valued at \$57,796,000 (16, p. 3).

When World War I broke out in 1914, Britain imposed a trade embargo on Germany. This halted American exports of food and cotton to Germany and imports of synthetic chemicals such as dyestuffs from Germany. Meanwhile, the U.S. was exporting munitions to Britain and France. As a result, while U.S. production of munitions soared, the American textile industry felt the ramifications of trade restrictions “[suffering] from a dye famine” (15, p. 261). “The last German-made dyes arrived in the US through normal [direct] channels at the end of April 1915” (12, p. 42). The Revenue Act of September 8, 1916 revised the Tariff Act of 1913, adding 5 cents per pound on coal-tar dyes and 2.5 cents per pound on intermediates with the hope that by 1917 the domestic output of dyes would about equal the pre-war imported quantity (16, p. 2). With high

consumer demand and Germany no longer a competitor, this was the opportune time for the U.S. to develop a domestic dyestuffs industry.

Foundations of Coal-tar Chemistry at DuPont

During the early years of World War I, DuPont was exclusively concerned with the production of munitions for the Allies. “[The] U.S. Army Ordnance Department estimated that DuPont ‘supplied over 40 per cent of the standard explosives used on the Allied side’” (14, p. 169) throughout the war. The raw materials that are required for smokeless-powder production are extracted from coal-tar. Chemicals that are required for dyestuffs are also based on coal-tar derivatives. It was their expertise in smokeless-powder production that gave DuPont an advantage in establishing a dyestuff industry.

Production of DuPont’s explosives used ammonia and aromatic organic compounds recovered from the volatile components of coal in the production of coke, as required in the steel industry. (Boiling out the volatile components of coal is also referred to as coking or destructive distillation.) Before the war, the aromatic organic byproducts of the American steel industry were largely discarded. Recovery of total coal coked in the steel industry was only 28% compared with 80% recovery during the formation of the dye industry (2, p. 1322). Before the war, materials such as toluene and diphenylamine were imported (14, p. 170). To synthesize TNT, trinitrotoluene, toluene is nitrated by an electrophilic aromatic substitution where an electron-rich nitronium ion (from nitric acid) in the presence of sulfuric acid attacks toluene (17, p. 347). To prevent or slow down self-decomposition, diphenylamine is a stabilizing chemical added to smokeless gunpowder. Starting in 1908, DuPont imported this stabilizer from Germany. “With the

onset of the war, DuPont chemists developed an improved process to make [diphenylamine] that was similar in structure to dyestuffs' intermediates (14, p. 170).

Coal-tar is formed as a product of destructive distillation of bituminous coal. In this process, the coal is heated in a cast-iron retort shut off from contact with air. This heating produces coal-tar that is subsequently partly dissolved in water. The constituents of coal-tar may be divided into three categories: hydrocarbons, phenols, and nitrogenous compounds. Separation of the constituents from coal-tar depends upon the selective results of fractional distillation (8, p. 7). The first distillate is separated into five fractions shown in Table 1 "These fractions are: first runnings, light oils, carbonic oil, creosote oil and anthracene oil. The first runnings consist of benzene, toluene, and xylene. Carbolic oils give phenol, cresol and naphthalene. And the anthracene oil primarily contains anthracene" (8, p.9).

Table 1: Fractions of coal-tar distillates (8, p. 11-12)

First runnings, or "first light oil"	to 105° C.
Light oil	to 210° C.
Carbolic oil	to 230° C.
Creosote oil	to 270° C.
Anthracene oil, or "green oil"270°-400° C.

From the first distillate, shown in Table 1, further distillations are done to produce more fractions. Appendix I shows the large number of compounds that can be fractioned from continuous distillation of coal-tar and their respective melting and boiling points. The different chemical compounds can be separated based on differences between their boiling points.

Building DuPont's Dye Industry

Although DuPont had extensive knowledge of coal-tar processing for smokeless-powder production, development of the synthetic-chemical industry presented many challenges. From their experience in the powder industry, DuPont had the technology to extract aromatic products from coal-tar. But the US was inexperienced in organic synthesis of the colored chemicals from the aromatic extracts. DuPont built what is now known as the Jackson Laboratory at Deepwater Point, opposite Wilmington on the New Jersey side of the Delaware River (7, p. 288).

Initially, DuPont started research and production of black, sulfur dyes due to high consumer demand; for example, Immedial Black V (formation shown in Appendix II). Their first experience in the new industry was not rewarding. They faced problems with reproducibility of product-color when scaling-up the newly learned chemistry, often producing off-shade batches (7, p. 290). DuPont's problems were due to inadequate education of American chemists concerning dye synthesis: "[many] of the recruits were fresh from the classroom. Textbooks had told them little or nothing of dye synthesis. [Suitable] apparatus was lacking, and could not be bought" (7, p. 289).

DuPont looked to Britain for help, sharing information with the Levinstein firm in Manchester, England (9, p. 60). But most of the chemical know-how was based in Germany. The U.S. sought out German patents on dyestuffs based on coal-tar intermediates; in October 1917, Congress passed the Trading-with-the-Enemy Act, and the Office of Alien Property was established (12, p. 43). This act granted DuPont access to the German patents through the Federal Trade Commission. The patents were written

for chemists with experience in the industry. Even with the patents, DuPont was unable to improve their troubled dye production.

In 1920, Dr. Elmer K. Bolton, the director of dye research at DuPont, hired four Ph.D.s from Bayer: Dr. Joseph Flachslaender, Dr. Otto Runge, Dr. Max Engelmann and Dr. Heinrich Jordan. DuPont offered each chemist \$25,000 per year, which far exceeded their German salaries. With the help of the German chemists, the dye industry in the US finally made progress. Table 2 shows how the price of relevant intermediates and dyes varied for imported versus domestically produced materials. Prices for 1913 (data obtained from the War Industries Board report) represent amounts paid by domestic consumers for imported materials. Prices for 1917, 1921, and 1936 are average amounts for sales from domestic production (data obtained from the US Tariff Commission). Table 2 focuses on prewar (1913), war (1917), and postwar (1921 and 1936) time periods.

Table 2: Comparison of domestic prices of selected intermediates and dyes in 1913,1917,1921 and 1936 [\$/pound] (16, p. 4)

Product		Imported	Domestic		
		1913	1917	1921	1936
Coal-tar intermediates:	Benzoic acid	\$0.23	\$2.28	(1)	\$0.30
	Dimethylaniline	0.19	0.59	0.54	0.20
	Phenol	0.11	0.37	0.14	0.10
Classified dyes:	Sulfur Black	0.22	0.55	0.38	0.28
	Indigo	0.18	1.42	0.45	0.16

Table 2 shows that in 1913 the U.S. was dependent on dye imports from Germany; by 1917, the U.S. was independent, producing dyes domestically. In the early years of the domestic industry, domestic dyes were significantly more expensive than imported dyestuffs. These high prices were a result of start-up costs of the new industry.

By 1936 the domestic industry was established and dye prices had declined to the prices of imported dyes in 1914.

In the early 1920s, the U.S. increased tariffs on chemical imports to prevent Germany from reclaiming their prewar dominant position in the dye market (10, p. 61). The Tariff Act of 1922 required that rates on all dutiable coal-tar products be based on the American selling price of any similar competitive article produced in the US. The U.S. dye industry flourished in the highly protected market: “In the U.S. during 1920, some one-hundred factories produced 88 million lbs. of dyes, fifteen times the output in 1914” (12, p. 43). Imports in 1921 and later years were largely noncompetitive specialty items used for further processing in branch factories. Exports consisted chiefly of standard dyes produced in large quantities. The principal dyes exported were indigo and sulfur-black (16, p. 2). Table 3 and Table 4 show the rapid growth of domestic coal-tar products that were strongly influenced by protective tariffs.

Table 3: Coal-tar products: Comparison of production, imports, and exports by quantity [in thousands of pounds] for 1917, 1921, 1929 and 1936 (16, p. 3)

Coal-tar Products		1917	1921	1929	1936
Production	Intermediates	322,746	70,900	354,488	509,706
	Dyes	45,977	39,009	111,422	119,523
Imports for Consumption	Intermediates	919	1,455	4,234	1,741
	Dyes	3,869	3,631	7,317	3,769
Exports	Intermediates	(1)	(1)	2,809	2,939
	Dyes	(1)	(1)	34,130	17,178
% Production	Intermediates	99.7%	98.0%	98.8%	99.7%
	Dyes	92.2	91.5	93.8	97.0

Table 4: Coal-tar products: Comparison of production, imports, and exports by value [in thousands of dollars] for 1917, 1921, 1929 and 1936 (16, p. 3)

Coal-tar Products		1917	1921	1929	1936
Production	Intermediates	\$106,967	\$17,725	\$67,353	\$71,359
	Dyes	57,796	32,377	47,911	64,542

Imports for Consumption	Intermediates	125	414	1,376	1,736
	Dyes	3,722	5,086	8,155	5,698
Exports	Intermediates	(1)	(1)	418	539
	Dyes	11,709	5,067	7,279	6,081

As shown in Table 3 and Table 4, United States' domestic dye production increased after the war. The production was highly dependent on tariff protection from the competing German imports. The 1922 tariff had a clear effect on dye production. In the early years of production, the domestic dye industry required protection from the U.S. government production to be competitive with Germany. As shown in Table 2, in 1921 the price of dye produced in the US was significantly more expensive than that of the imported product. Thus, the US government was instrumental in the formation of a domestic dye industry by supporting companies like DuPont in the early stages of development.

DuPont spent \$43 million before showing a profit. The early U.S. dye production pioneers were Du Pont, Allied and American Cyanamid. In 1938, Dow and GAF joined in. In the 1960s 50-60% of all U.S. manufacturing was in the hands of four U.S. companies. However, today there are no surviving major U.S. dye companies. The Swiss and German-backed companies predominate (Ciba, and Clariant, Dystar and Bayer). Most of the international companies do limited production in the U.S. and most production is where environmental laws are less stringent (11, p. 510). DuPont has moved onto a different area of the synthetic-chemistry industry.

DuPont's Transition to Today

Deepwater Point, the center of DuPont's dye operations, evolved into the site of DuPont's chemical production. Tetraethyl lead (TEL), a chemical used as an anti-knock agent in gasoline, was produced at Deepwater. During the 1950s and 1960s, Deepwater was the largest chemical plant in the U.S. with 6,500 employees working in more than 500 buildings. Although dye production ended in 1980, today, Deepwater remains central in DuPont's production of chemical intermediates (3). Today, The First Chemical Corporation, a DuPont company, is the second largest producer of aniline intermediates and the only U.S. producer of Nitrotoluene intermediates and derivatives (4). Aniline intermediates are used to manufacture rigid foam for automotive and construction industries, and also used to produce Kevlar® aramid fibers for tires, sails and body armor. Nitrotoluenes are used in sealants, fillers, dyes, herbicides, and as detergent additives (4).

Success in the dye industry led DuPont to extend research to other materials; by the 1930s, DuPont's synthetic-chemical industry was responsible for DuPont's polymer expertise, producing nylon, neoprene, Teflon, Kevlar and Lycra. Later, DuPont's synthetic-chemistry research was expanded to antioxidants for gasoline and to rubber, insecticides, herbicides, seed treatments, fluorochemicals, lubricants, polymers, cleaners and disinfectants. DuPont remains the world's leading producer of nylon, chemical intermediates, polymers, and textile fibers (6).

Conclusion

The synthetic-organic-chemical industry in the U.S. was built after 1914 for the production of dyes. The outbreak of World War I and ensuing blockade of German ports showed the U.S. that it needed a domestic dye industry. DuPont's leap into the dye industry had a strong foundation in coal-tar chemistry as required for DuPont's long-established smokeless-powder production. Government protection of U.S. domestic dye production through pertinent tariffs was necessary for formation of that industry. DuPont has since expanded within the synthetic-organic chemical industry, focusing more on materials and no longer on the production of dyes. DuPont's chemical industry provides employment for scientifically trained men and women; that requirement provides an incentive for pertinent academic training (7, p. 294). "By the mid-1940s, two-thirds of the [DuPont's] Organic Chemicals Department's products were directly traceable to prior dye-related research" (5). Through the formation of the dye industry, DuPont built a synthetic chemical industry that we depend on today.

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Appendix I: Coal-Tar Components Distillation Information (8, p. 11-12)

CONSTITUENTS OF COAL-TAR

1. HYDROCARBONS

	Formula.	Melting-point.	Boiling-point.
Crotonylene	C_4H_6	Fluid	20° C.
Hydrocarbons (ethylene series)	C_nH_{2n}
Hydrocarbons (methane series)	C_nH_{2n+2}
Benzene	C_6H_6	6° C.	80.4° C.
Toluene	C_7H_8	Fluid	110.3° C.
<i>o</i> -xylene	C_8H_{10}	-28° C.	142° C.
<i>m</i> -xylene	C_8H_{10}	-54° C.	139° C.
<i>p</i> -xylene	C_8H_{10}	15° C.	138° C.
Styrene	C_8H_8	Fluid	146° C.
Mesitylene	C_9H_{12}	"	163° C.
Pseudocumene	C_9H_{12}	"	166° C.
Naphthalene	$C_{10}H_8$	79° C.	218° C.
Methylnaphthalene	$C_{11}H_{10}$	<i>a</i> -20°, <i>b</i> 33° C.	242° C.
Diphenyl	$C_{12}H_{10}$	71° C.	254° C.
Acenaphthene	$C_{12}H_{10}$	95° C.	277° C.
Fluorene	$C_{13}H_{10}$	113° C.	295° C.
Phenanthrene	$C_{14}H_{10}$	99° C.	340° C.
Fluoranthrene	$C_{15}H_{10}$	110° C.	above 360° C.
Anthracene	$C_{14}H_{10}$	213° C.	351° C.
Methylanthracene	$C_{15}H_{12}$	190° C.	above 360° C.

	Formula.	Melting-point.	Boiling-point.
Pryene.....	$C_{16}H_{10}$	149° C.	260° (60mm.) C.
Chrysene.....	$C_{18}H_{12}$	250° C.	448° C. (?)
Picene.....	$C_{22}H_{14}$	364° C.	520° C.

2. OTHER NEUTRAL BODIES

Carbon disulphide.....	CS_2	Fluid	47° C.
Ethyl alcohol.....	C_2H_5OH	-130° C. (?)	78.3° C.
Acetonitril.....	C_2H_3N	-41° C.	81.6° C.
Thiophene.....	C_4H_4S	Fluid	84° C.
Thiolenene.....	C_5H_6S	"	113° C.
Thioxene.....	C_6H_8S	"	134° C.
Benzonitrile.....	C_7H_5N	"	191° C.
Phenylthio carbimide..	C_7H_5NS	"	220° C.
Carbazole.....	$C_{12}H_9N$	238° C.	351° C.
Phenyl-naphthyl carba- zole.....	$C_{16}H_{11}N$	330° C.	above 440° C.
Coumarone.....	C_9H_6O	Fluid	169° C.

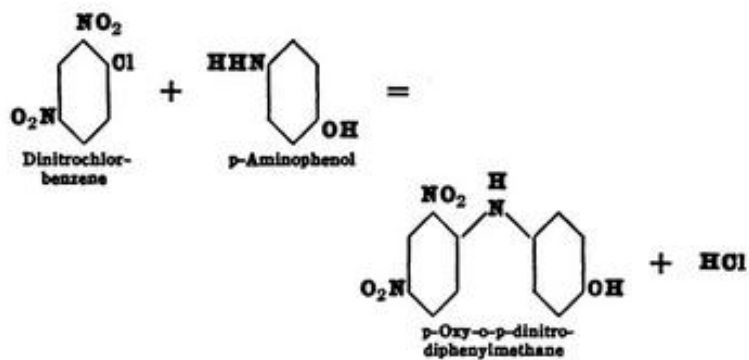
3. BASES

Pyridine.....	C_5H_5N	Fluid	114.8° C.
Pyrrol.....	C_4H_5N	"	131° C.
Picoline.....	C_6H_7N	"	130° C.
Lutidine.....	C_7H_9N	"	157° C.
Collidine.....	$C_8H_{11}N$	"	171-172° C.
Aniline.....	C_6H_7N	-8°	184° C.
Quinoline.....	C_9H_7N	"	239° C.
Quinaldine.....	$C_{10}H_9N$	"	247° C.
Acridine.....	$C_{13}H_9N$	110° C.	above 360° C.

4. PHENOLS

Phenol.....	C_6H_6O	43° C.	183° C.
<i>o</i> -cresol.....	C_7H_8O	31° C.	188° C.
<i>p</i> -cresol.....	C_7H_8O	36° C.	198° C.
<i>m</i> -cresol.....	C_7H_8O	4° C.	201° C.
<i>α</i> -naphthol.....	$C_{10}H_8O$	95° C.	278-280° C.
<i>β</i> -naphthol.....	$C_{10}H_8O$	122° C.	286° C.
Xylenols and other high boiling phenols.....			

Appendix II: Formation of Immedial Black V (8 p. 396)



The fusion of this product with sulphur and sodium sulphide yields the immedial black V.