

# The Chemistry and Manufacture of Vat Dyes

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## I) Introduction

Vat dyes, which include indigo and anthraquinone-based dyes, are chemically complex dyes which are insoluble in water. They must first be reduced to the leuco form in an alkaline solution of sodium hydrosulfite before application to the cotton or rayon fiber. Air oxidation fixes the dye strongly on the fiber, resulting in excellent wash-fastness and light-fastness. The vat dyes were one of the most significant textile dye inventions in the 20<sup>th</sup> century.

Indanthrene blue was the first anthraquinone vat dye, synthesized by René Bohn at BASF in Germany in 1901. He used the synthetic indigo reaction conditions with 2-aminoanthraquinone, fusing it with caustic potash, to obtain the colorant. By 1906, Bayer had introduced the first vat red and marketed a range of colors under the Alcol brand. The United States imported vats from Germany because domestic production was hindered by German patent protection, the lack of sufficient anthracene (the source of anthraquinone), inadequate technical expertise of American chemists, and the large investment needed for organic solvent operations, specialized equipment, and explosion proof manufacturing buildings.

A breakthrough occurred in 1917 when government chemists in Washington, DC developed a process to manufacture anthraquinone from readily available coal-tar naphthalene and benzene. Vapor-phase oxidation of naphthalene gave phthalic anhydride, which was condensed with benzene to form 2-benzoyl benzoic acid (Friedel-Crafts reaction), followed by ring closure with sulfuric acid to afford anthraquinone.

Sulfonation of anthraquinone gave 2-anthraquinonesulfonic acid, named silver salt because of the silvery sheen of its crystals. Reaction of silver salt with ammonia in an autoclave at 200 °C and pressures of up to 1000 psi yielded 2-aminoanthraquinone, a source of several vat dyes. The use of toluene instead of benzene gave 2-methylanthraquinone, the starting material for vat orange dyes. Far more significant, however, was the versatile 1-aminoanthraquinone. This required mercury-catalyzed sulfonation of anthraquinone, to afford 1-anthraquinonesulfonic acid (known as diamond salt), followed by arsenic-catalyzed amination. Diamond salt was a source of olive greens, browns, grays, etc. This often involved many chemical synthesis steps, apart from the physical steps of separating, drying, and finishing. Vat dye processes included the production of other intermediates, such as benzanthrones, in which an additional aromatic ring was added on to anthraquinone. (Reference 1)

In 1919 Du Pont accomplished the first successful commercial production of anthraquinone vat dyes in the United States. One year later, a range of colors was available, marketed by Du Pont under the trade name Ponsol. In 1927 the National Aniline & Chemical Company, a subsidiary of Allied Chemical & Dye Corporation, entered the market with Carbanthrene vat dyes. General Aniline and Film Corporation and the Calco Chemical Division of American Cyanamid soon followed with their own

ranges of vats. In 1928 the production of vat dyes, excluding indigo, grew to 6.3 million pounds, representing almost 7 per cent of the total dye production in the U.S.

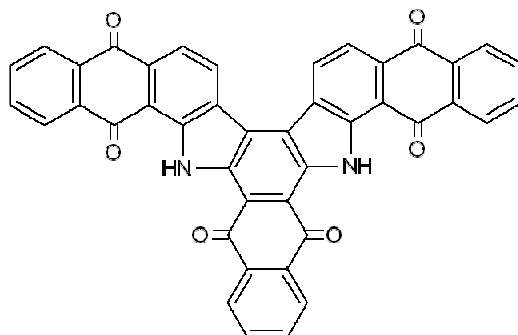
By the 1950s U.S. manufacturers were producing a rainbow of vat dye colors, in either paste or powder forms, as shown in **Table 1**. (References 2, 3, 4, 5, 6):

**Table 1. Common Vat Dyes**

<b>Color Index (CI) Name</b>	<b>CAS No.</b>
Vat Yellow 2	129-09-9
Vat Yellow 4	128-66-5
Vat Orange 1	1324-11-4
Vat Orange 9	128-70-1
Vat Orange 15	2379-78-4
Vat Orange 2	1324-35-2
Vat Orange 3	4378-61-4
Vat Blue 5	2475-21-2
Vat Blue 14	1324-27-2
Vat Blue 20	116-71-2
Vat Blue 6	130-20-1
Vat Blue 18	1324-54-5
Vat Green 1	128-58-5
Vat Green 2	25704-81-8
Vat Brown 3	131-92-0
Vat Brown 1	2475-33-4
Vat Red 1	2379-74-0
Vat Red 10	2379-79-5
Vat Red 13	4203-77-4
Vat Violet 9	1324-17-0
Vat Violet 1	1324-55-6
Vat Violet 13	4424-87-7
Vat Green 8	14999-97-4
Vat Black 27	2379-81-9
Vat Green 3	3271-76-9
Vat Black 25	4395-53-3
Vat Black 34	12271-03-3

## II) Manufacture of Common Vat Dyes

### 1) CI Vat Brown 1 CAS 2475-33-4 (Fig. 1)

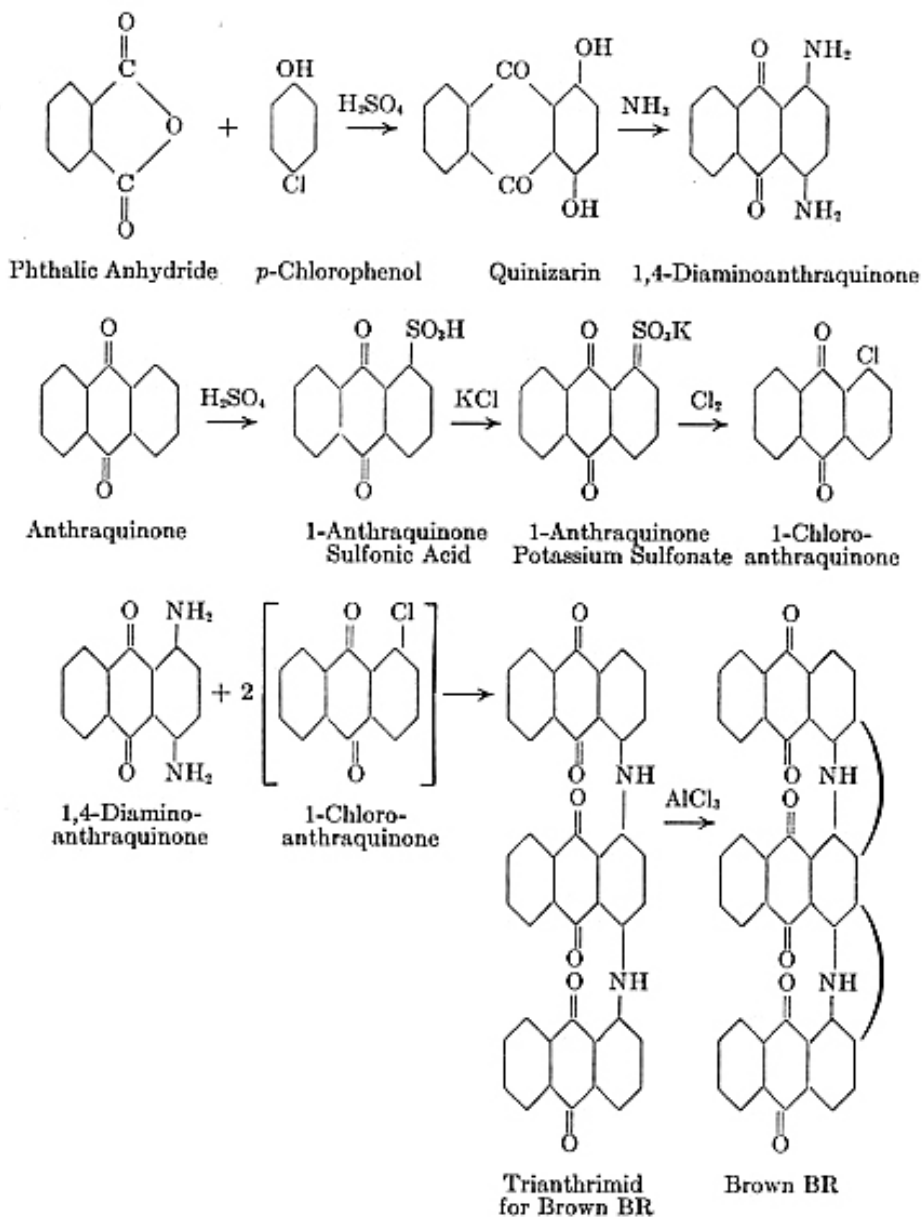


**Fig. 1 CI Vat Brown 1**

The large volume vat dyes eventually became commodity products available from several suppliers. The know-how was freely available after World War II, when the British and American governments published the BIOS and FIAT intelligence reports that detailed the chemical processes and equipment used by the leading German dye manufacturers.

CI Vat Brown 1, a carbazole derivative of anthraquinone, is a representative example of the complexity of vat dye manufacture. Ciba made the dye, known as Cibanone Brown BR, at their plant in Toms River, New Jersey and published details of the process in 1954, which are described below (Reference 7).

Two different intermediates were first prepared and then reacted together to form the dye. The chemical steps are shown below (**Fig. 2**):



**Fig. 2 Chemical Synthesis of CI Vat Brown 1**

Phthalic anhydride and *p*-chlorophenol were reacted in sulfuric acid to form quinizarin. The quinizarin was aminated to yield 1,4-diaminoanthraquinone.

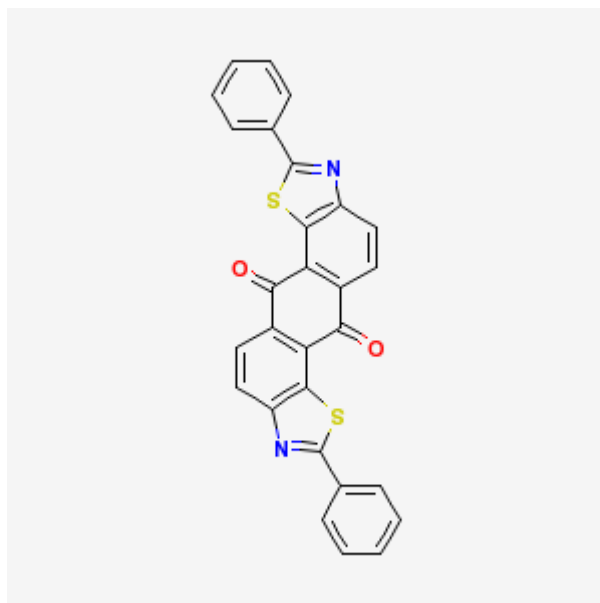
The conversion of anthraquinone to 1-anthraquinonesulfonic acid required the use of the catalyst mercuric sulfate to direct the sulfonation to the number 1 position on the anthraquinone ring. Chlorination formed 1-chloroanthraquinone.

The next stage was the condensation of the two intermediates in the presence of a copper catalyst to form the trianthrimid of Brown BR (1,4-(dianthraquinoylamino)-anthraquinone). Carbazolation was carried out in pyridine and aluminum chloride. The seven step process for Brown BR had an estimated overall yield of only 19 percent. Low

chemical yields and the use of hazardous raw materials and solvents made vat dyes the most highly polluting class of dyes manufactured.

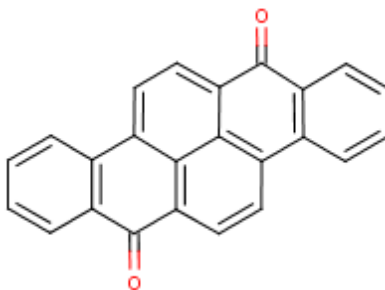
**2) CI Vat Yellow 2 CAS No. 129-09-9 (Fig. 3)**

The first stage in the manufacture of this dye was the preparation of the intermediate 2,6-diaminoanthraquinone., which was then reacted in naphthalene solvent with benzotrichloride, sulfur, and cuprous chloride catalyst . Naphthalene was recovered by steam distillation in the venuleth dryer. (References 8-10)



**Fig. 3 CI Vat Yellow 2**

**3) CI Vat Yellow 4 CAS No. 128-66-5 (Fig. 4)**

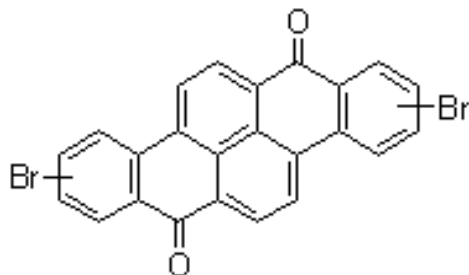


**Fig. 4 CI Vat Yellow 4**

This dye is a representative of the dibenzopyrenquinone class. It was prepared from 1,5-dibenzoylnaphthalene, which was made by Friedel-Crafts acylation (benzoylation) of naphthalene. The 1,5-dibenzoylnaphthalene was recrystallized in monochlorobenzene and then fused in a melt of aluminum chloride to form Vat Yellow 4. The dye could be

further purified by bleaching with sodium hypochlorite to give a brighter shade.  
(Reference 11)

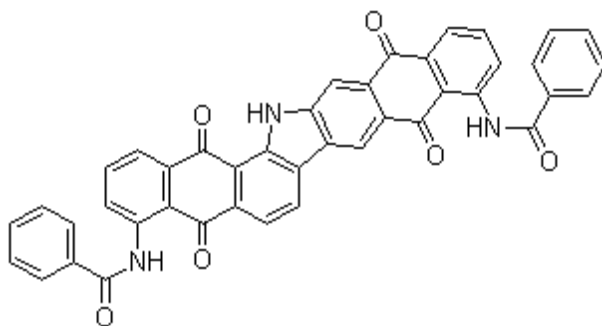
**4) CI Vat Orange 1 CAS No. 1324-11-4 (Fig. 5)**



**Fig. 5 CI Vat Orange 1**

This dye was made by brominating Vat Yellow 4 in an aluminum chloride melt.  
(Reference 12)

**5) CI Vat Orange 15 CAS No. 128-70-1 (Fig. 6)**



**Fig. 6 CI Vat Orange 15**

CI Vat Orange 15 is a member of the anthrimidocarbazole class and was prepared by the reaction of the intermediates 1-amino-5-benzoylaminoanthraquinone and 1-benzoylamino-5-chloroanthraquinone followed by ring closure. The synthesis required mercury. (References 13-17)

6) CI Vat Blue 20 CAS No. 116-71-2 (Fig. 7)

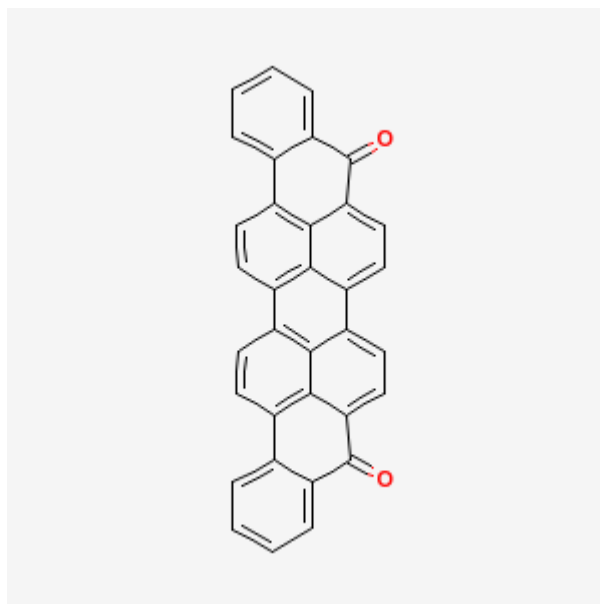


Fig. 7 CI Vat Blue 20 (Dibenzanthrone or Violanthrone)

The first step was the preparation of benzanthrone (Fig. 8) by the reaction of anthraquinone with glycerol in the presence of iron, which is the reducing agent:

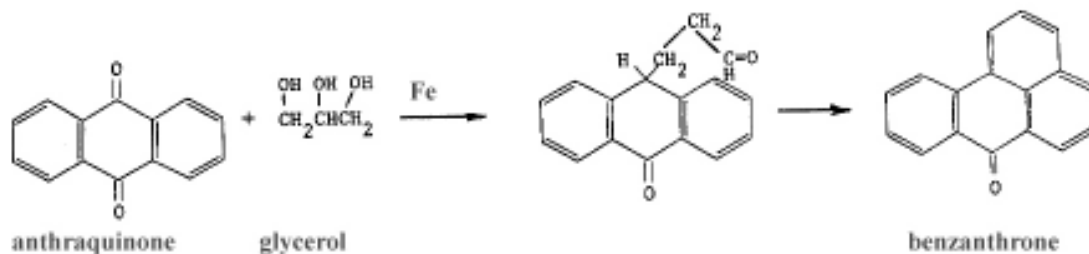


Fig. 8 Synthesis of Benzanthrone

Benzanthrone was next converted to dibenzanthrone, also known as violanthrone, by alkali fusion. (References 18-19)

7) CI Vat Green 1 CAS No. 128-58-5 (Fig. 9)

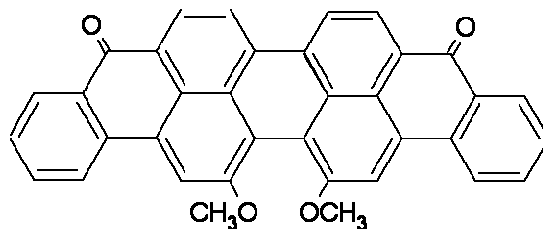


Fig. 9 CI Vat Green 1 (Jade Green)

Treatment of benzanthrone with alcoholic caustic potash gave the 2:2'-dibenzanthronyl intermediate. (Reference 20) The 2:2'-dibenzanthronyl was oxidized with manganese dioxide to form dihydroxy dibenzanthrone. The last step involved methylation of the dihydroxy dibenzanthrone. (Reference 21)

### III) Waste Streams of Vat Dye Manufacture

Synthetic dye manufacture requires a series of chemical reactions to form the dye followed by finishing procedures to produce a dry powder or paste for use by customers. (Fig. 10) Customers preferred the easier to handle paste form.

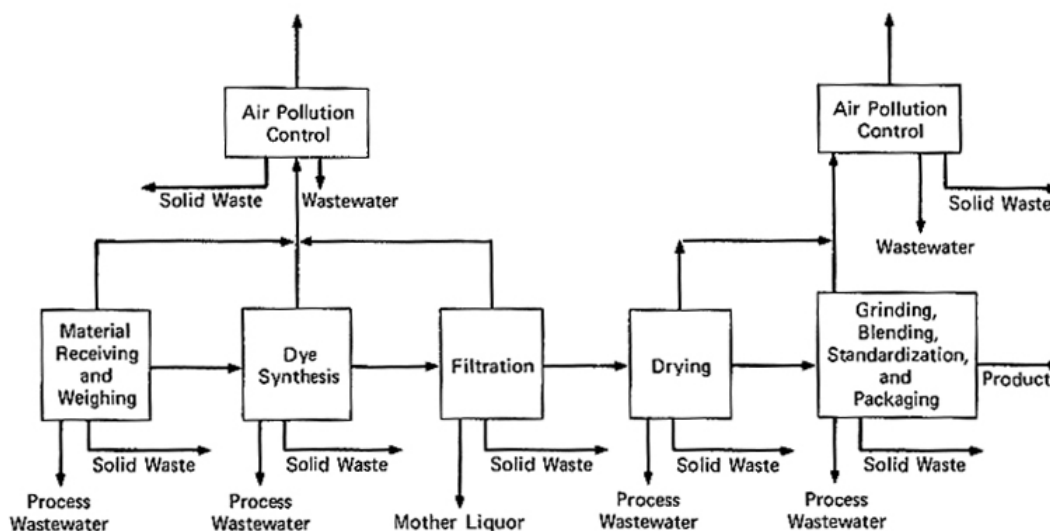


Fig. 10 Process Flow Schematic for Manufacture of Synthetic Dyes (Reference 22)

Each chemical and physical step in the process can generate process wastewater, solid waste and air emissions. The anthraquinone based vat dyes require more synthetic steps than the acid, basic, direct, disperse and reactive dye classes. The multiple chemical reactions increase the consumption of raw materials, resulting in vat dyes having the highest ratio of raw materials to finished dye as compared to the other dye classes. This ratio is reported as 4.8:1 for the vat dye production of German companies and as 5.5:1 for the vat dye production by Ciba in Toms River, New Jersey in 1954. (Reference 23) The high raw material to dye ratio makes vat dyes the leading generator of wastewater and hazardous waste compared to other dye classes. Wastewater from the manufacture of vat dyes is on the order of 8,000 liters per kg of product compared to a maximum of 700 liters per kg for the other dye classes. (Reference 24)

The most significant material losses in dye production come from incomplete chemical reactions. The yield of the various reactions discussed in section II) above ranges from 39 to 98 percent, with an average of only 79 percent of theory. Some of the vat dyes require five or more synthetic steps. If each step averages a 79 percent yield, the overall

yield of a five step process is only 31 percent of theory. If seven steps are required, which is the case for Vat Brown 1, the overall yield is only 19 percent of theory.

Most of the raw materials used in the manufacture of vat dyes are hazardous since they are ignitable, corrosive, or toxic. The low yields result in hazardous chemicals in the wastewater and in solid wastes such as solvent still bottoms and filtration clarification sludges.

The wastewater from vat dye synthesis will contain unreacted raw materials and byproducts which are soluble in addition to inorganic salts formed by neutralization. The heavy metal catalysts and reagents used in key intermediate steps, such as mercury, arsenic, copper and chromium, are primarily found in the wastewater as soluble salts, and can contaminate soil and groundwater if improperly treated or disposed of.

The acid, basic, direct, disperse, and reactive dye classes are generally manufactured in aqueous media. Vat dyes, however, require high boiling solvents in many of the intermediate steps, since temperatures over 200 deg. C are necessary to drive the reactions. The most common solvents are nitrobenzene, naphthalene and the chlorinated solvents chlorobenzene, 1, 2-dichlorobenzene (o-dichlorobenzene), and 1, 2, 4-trichlorobenzene (trichlorobenzene). (Reference 25) All of these solvents are hazardous chemicals with the potential of severe environmental contamination.

In the vat dye industry, the solvents can be recovered by collecting the mother liquor from the filtration step in a distillation vessel equipped with a condenser and receiver. However it is more common to use a venuleth (paddle) dryer. This is a horizontal rotary vacuum dryer used to obtain dry powder from wet cake or solutions and to recover the solvent at the same time. Steam is supplied to an exterior jacket and to a hollow shaft and paddles within the unit.

Solvent recovery generates still bottoms that must be removed from the equipment between batches in order to facilitate heat transfer. The tarry residue is scraped from the interior of the equipment and usually packed in drums for disposal. The spent solvent still bottoms from vat dye manufacture are listed as hazardous wastes by the RCRA (Resource Conservation and Recovery Act) regulation enacted by the EPA in 1976. The still bottoms may also contain unreacted raw materials and reaction byproducts.

Filtration operations also result in solid waste when off-specification intermediates or dyes are purified by recrystallization in solvents. Diatomaceous earth and activated carbon are typically added to the solution to adsorb the unreacted raw material or other impurities and to prevent blinding of the filter media. The filtration clarification sludge from vat dye operations will likely contain RCRA listed hazardous wastes including organic chemicals and heavy metals.

Empty raw material containers represent another source of potentially hazardous solid waste disposed of by dye manufacturers. The chemicals can stick to the walls of the container or to the paper or plastic liners.

It was common practice in the dye industry to pack the spent still bottoms and filtration sludge wastes in steel drums. Prior to the RCRA law in 1976, dye producers usually buried these hazardous waste drums on site or arranged for off-site disposal. Many of these disposal locations became Superfund sites or state hazardous waste sites due to the serious contamination of soil and groundwater from the drummed wastes.

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