Contemporary methods for production of Prussian blue

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Abstract. Prussian blue, a blue-coloured pigment, has found a wide application in various branches of production, including such industries as construction and transport, where Prussian blue is applied as a coloured coating, and also in agriculture and medicine. A typical technological process for production of Prussian blue includes nucleation, enlargement of formed crystals, aggregation of formed crystals, and, finally, recrystallization followed by further oxidation, rinsing of impurities and drying. A typical technological process for production of Prussian blue is observed, its features are studied, and the influence of chemical components on the properties of the obtained pigment are examined. Recommendations on the mole ratio and concentrating of chemical components are given. The pigment produced by the given recommendations is superior in quality to foreign counterparts.

1. Features of the technology for producing Prussian blue

Prussian blue, or iron blue, is a pigment of a colour varying from dark-blue to blue, sometimes having a reddish tint [1]. Chemically, Prussian blue is ferric hexacyanoferrate (II), or a mixture of ferric ferrocyanide with either alkali metals (e.g. potassium, and sodium), or ammonium, with the formula $\text{Fe}_3\left[\text{Fe}^{++}(\text{CN})_6\right]_2\cdot x\text{Me}_4\left[\text{Fe}^{+++}(\text{CN})_6\right]_n \cdot m\text{H}_2\text{O}$, having $x = 0.3...0.8$ and $n = 0.03...0.17$.

As stated in [2-7], Prussian blue is the first purely synthetically produced pigment. It is less expensive, more available, and more easily produced as compared to ultramarine or other blue-coloured pigments [8-11]. Prussian blue is a very stable chemical compound except for being labile in alkaline environment. Nowadays, not only Prussian blue is used as a pigment, but it also has other applications including electrochromic, sensors [12-16] and medical substances, e.g. poison antidotes [17-19].

To obtain Prussian blue, such raw materials as ferrocyanide, ferrous sulphate, hydrochloric acid and potassium chlorate of technical qualification (i.e. with the ratio of the yielded reagent less than 95%) are applied [20]. The technological process for producing Prussian blue from the above-listed raw materials includes four kinetic stages [21-23]:

1. Formation of crystallization nuclei with the formation of sediment resembling white dough;
2. Growth of the crystallization nuclei into crystals of a bigger size;
3. Sintering of crystals into larger particles during heat treatment;
4. Recrystallization of formed particles into pasteous pigment as a result of oxidation.

According to the above-mentioned technology shown in figure 1, at the first stage, white sediment is yielded as a result of the interaction of green vitriol with potassium ferrocyanide, with the following reaction proceeding:
$2\text{FeSO}_4 + 1.8\text{K}_4\text{Fe( CN)}_6 \rightarrow \text{Fe}_2\left[\text{Fe( CN)}_6\right]0.8\text{K}_4\text{Fe( CN)}_6 + 2\text{K}_2\text{SO}_4$

At the second stage, particles of ferric ferrocyanide, treated at high temperatures in the reaction device for a certain time, can aggregate, i.e. sinter into large conglomerates, while moving, which reduces the dispersibility of Prussian blue.

At the second and third stages, just before the oxidation process, the white sediment is subject to heat treatment, viz. boiling in acidic environment. After the boiling is completed, the yielded sediment is cooled either to a temperature of 60...70 °C with the application of potassium chlorate, or to a temperature of 20...30 °C with the application of potassium dichromate. The application of potassium imparts a light blue colour to the obtained Prussian blue.

Finally, at the fourth stage, the application of easily air-oxidable white sediment obtains Prussian blue, with the following reaction proceeding:

$6\left\{\text{Fe}_2\left[\text{Fe( CN)}_6\right]0.8\text{K}_4\text{Fe( CN)}_6\right\} + 2\text{KClO}_3 + 6\text{H}_2\text{SO}_4 \rightarrow$

$\rightarrow 3\left\{\text{Fe}_4\left[\text{Fe( CN)}_6\right]0.6\text{K}_4\text{Fe( CN)}_6\right\} + 2\text{KCl} + 2\text{K}_2\text{SO}_4 + 6\text{H}_2\text{O}$

To transform the yielded white-coloured sediment into the blue-coloured one, such oxidizing agents as potassium chlorate or potassium dichromate are applied [24,25]. When the oxidation process is completed, the obtained Prussian blue is rinsed with water from impurities, and with a surfactant fed, the rinsing process accelerates. Finally, the rinsed Prussian blue is dried in the steam dryer and, after feeding through the screw conveyer and elevator, is ground in the grinding device [26].

In manufacture, Persian blue is produced as pastaceous aqueous solution of a filmogen. After the filtration of Prussian blue is completed, the filmogen and the surfactant are fed to the yielded aqueous paste, and the formed mixture is stirred. Particles of Prussian blue, initially moistened with water, are subsequently subject to moistening with the filmogen. Water which is not mixable with the filmogen is subject to vacuum separation and removal. The yielded paste is applied in the manufacture of paints and enamels. Besides, by using this method, the drying and grinding operations can be excluded from the technological process.

2. Proposals on increasing the efficiency of producing Prussian blue

Various studies of the production of Prussian blue have discovered the following features of its obtaining:

1. The structure of Prussian blue sediment significantly depend on iron (II) ions adsorbed because of the yielding of “white dough” on the surface of the sediment. With the presence of ferrocyanide ions in the solution, a sediment chemically similar to $\text{K}_4\text{Fe[ Fe( CN)}_6\]_6\}$ is yielded, and with the presence of iron (II) ions in the solution, a sediment of variable composition with the ratio of ions equal to $\text{Fr}^{2+}/\left[\text{Fe( CN)}_6\right]^{4-} = 1.1...1.3$, is also yielded.

2. The chemical composition of Prussian blue sediments during the obtaining process varies with the concentration of potassium ferrocyanide solution and the mole ratio of potassium ferrocyanide to ferrous sulphate.

3. The properties of Prussian blue pigment depend on the chemical composition and properties of the yielded sediments with the chain-sintered crystals and the developed surface, thus providing high filtration strength and rate. Such properties are attained at the concentration of potassium ferrocyanide solution in the range from 50 to 100 g/l with the mole ratio of potassium ferrocyanide to ferrous sulphate equal to 1.0:(1.33...1.10).
Figure 1. Technological process for obtaining Prussian blue: 1 – preparation devices for the feed solution, 2 – receiving tanks for the feed solution, 3 – filters, 4 – receiving tanks for the filtered solution, 5 – measuring tank, 6 reaction device, 7 – vacuum filters, 8, 13 – bins, 9 – electric hoist, 10 – steam dryer, 11 – screw conveyer, 12 – elevators, 14 – grinding device, 15 – pump, 16 – liquid counter.

In order to increase the production efficiency of Prussian blue and decrease the concentration of water-soluble salts in it, the interaction of the reagents is performed while feeding them into the cooking kettle at a pH ranging from 0.8 to 1.2, with the concentration of diluted alkali metal or
ammonium ferrocyanide salt ranging from 80 to 100 g/l, and that of ferrous salts ranging from 100 to 200 g/l. The oxidation process is performed at a pH ranging from 1.8 to 2.2.

To improve the dispersibility of Prussian blue and to simplify its production, ammonium persulphate is applied as an oxidizing agent with the mole ratio of ammonium persulphate to ammonium ferrocyanide equal to (0.3…0.5):1, and mole ratio of the amount of potassium ferricyanide to ferrous sulphate equal to 1.0:(1.1 ... 1.3).

The productivity of the cooking kettle used to produce Prussian blue is significantly increased by increasing the concentration of potassium ferrocyanide from 45...65 to 70...80 g/l, with the concentration of ferrous sulphate, potassium chlorate suitably adjusted, and, besides, by increasing the consumption of hydrochloric acid from 141 to 166 kg per 1 ton of finished product.

Based on the conducted research and industrial tests, there has been developed a method for modifying the surface of Prussian blue. According to the developed method, water-soluble salts of alkyl phosphates, viz. triethanolamine alkylphosphate based on either primary fatty alcohols of the C7-C12 fraction or secondary fatty alcohols of the C10-C20 fraction, are fed into the water to dilute the oxidized slurry. When the drying process is conducted during modification, the yielded pastes enable maintaining the process temperature below the decomposition temperatures of the introduced modifiers.

Prussian blue obtained according to the above-listed recommendations, is superior in quality to Prussian blue samples produced by the best foreign companies such as Siegle (Germany), Manoko (Manchester, UK). Based on the results obtained during the study and experimental confirmation, there has been developed a technological process for the production of Prussian blue with a capacity of 6000 tons/year.

3. Conclusions
The above-listed technological process allows us to make the following conclusions:
4. The production of Prussian blue is based on ferric ferrocyanide, ferrous sulphate, hydrochloric acid and potassium chlorate applied as raw materials.
5. The technological process for the production of Prussian blue consists of 4 steps and results in the obtaining of paste-like sediment of a white (without oxidation) or a blue (with oxidation by means of potassium chlorate or potassium dichromate) colour.
6. The properties of Prussian blue such as filtration intensity, dispersibility depend on the concentration and mole ratio of chemical ingredients and oxidizers.
7. The technological process for the production of Prussian blue allows the obtaining of high-quality pigment, which can be produced in big volumes.

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