Contemporary methods of production of pigments obtained from non-ferrous industrial waste

A V Vyboishchik¹, I L Kostiunina²

¹Automated Machine-Building Technology, South Ural State University, 76, Lenin Avenue, Chelyabinsk 454080, Russia
²Engineering and Computer Graphics, South Ural State University, 76, Lenin Avenue, Chelyabinsk 454080, Russia

E-mail: alex_vyb@list.ru

Abstract. The current article describes green pigments’ manufacturing and application problems. Verditer green, or green pigment, is a group or chemical compounds used in various branches of industry, especially in manufacturing paints used for decoration and restoration of engineering constructions and other buildings. The properties and methods of obtaining verditer green from industrial waste are presented with the properties of viridian and cobalt green taken as the examples of green pigments. The technology of obtaining chromium oxide III, chromium hydroxide III, cobalt green including the required equipment, is given with the focus on the calcination process, the chemical reactions are performed both in description and chemical formulae, the different methods of obtaining the pigments, depending on the demanded pigment’s colour, are offered, and the technical and chemical requirements for the raw material and the pigments’ compound are listed.

1. Introduction

Pigments, or finely dispersed water insoluble powders [1-3], have gained broad usage in various branches of industry, viz. in manufacturing enamels, paints, plastics, etc. Enamels and paints have gained broad application in civil engineering, especially in colouring and coating [4-8].

Russian pigment-producing industry, once having powerful manufacturing facilities, since 1991 has lost most of its enterprises with virtually no enterprises producing inorganic pigments remained by present. The few existing pigment producing enterprises built as long ago as in 1960…1970’s have significant disadvantages in equipment and production technology, viz.:

The low percentage of main chemical components in raw material due to unsatisfactory enrichment of mineral ores;

The low extraction ratio and the quality of obtained pigments due to low productivity equipment used for crushing raw materials before its processing;

The high loss rate of the raw materials and semiproducts while reagentizing due to low productivity of machines used for slurry mixing and reagent crushing;

The high energy cost and low pigment quality of raw materials and semiproducts after the process of calcination due to the usage of rotary kilns not providing equable layer-through heating of the product;

The low quality of the calcined product due to the usage of ball, roll and other types of crushers.
In this regard, in order to eliminate the above-mentioned disadvantages and ensure the high quality of produced pigments, it is necessary to apply low-waste technologies for processing raw materials and semi-products.

2. Properties of chromium-containing pigments and methods for their preparation

The group of verditer green chromatic pigments consists of a large number of chemical compounds widely diverse in composition and properties, viz. metal oxides and hydroxides, salts, which properties and methods for preparation are given below.

Chromium-containing pigments include the following green-coloured chemical compounds: chromium oxide III (Cr$_2$O$_3$), chromium hydroxide III (Cr$_2$O$_3$·nH$_2$O), chromium phosphate (CrO$_4$), chromium silicate and some spinel-type compounds [9,10]. Chromium compounds with constant chemical composition change their colours in a wide range with their dispersion, temperature and concentration. The change in chromium hydrates’ colour with the composition of crystalline hydrates and the crystallization temperature is given in Table 1.

| The composition of the dried sediment at a temperature of, °C | Crystallization temperature, °C | The colour of the pigment |
|---------------------------------------------------------------|-------------------------------|--------------------------|
| Cr(OH)$_3$·3H$_2$O                                             | 640                           | Blue                     |
| Cr(OH)$_3$·2,15H$_2$O                                          |                               | Green with a blue tinge   |
| Cr(OH)$_3$·2,55H$_2$O                                          |                               | Green with a blue tinge   |
| Cr(OH)$_3$·2,75H$_2$O                                          | Cr(OH)$_3$·1,95H$_2$O         | Green with a blue tinge   |
| Cr(OH)$_3$·1,8H$_2$O                                           | Cr(OH)$_3$·1,1H$_2$O          | Dark green               |

Green pigment is olive-green coloured chromium oxide III Cr$_2$O$_3$ having tinges from yellowish to bluish.

Such pigment can be obtained by means of either the thermal or the combined method. The thermal method reducing potassium or sodium dichromate over sulphur, coal, gypsum or ammonium salts is more widely used.

Furnace burden is prepared by mixing the above-mentioned components, with subsequent calcination, with the following reactions (1-4) occurring:

$$K_2Cr_2O_7 + S \rightarrow Cr_2O_3 + K_2SO_4;$$
$$K_2Cr_2O_7 + 2C \rightarrow Cr_2O_3 + K_2CO_3 + CO;$$
$$K_2Cr_2O_7 + 2NH_4Cl \rightarrow Cr_2O_3 + 2KCl + 4H_2O + N_2;$$
$$K_2Cr_2O_7 + CaSO_4 \rightarrow Cr_2O_3 + K_2SO_4 + CaO + 1,5SO_2.$$
Na₂Cr₂O₇ + 6S + 7H₂O → 4Cr(OH)₃ + 3Na₂S₂O₃ + 2NaOH.

The resulting sediment of chromium hydroxide III is washed off with hot water and calcined at 800 to 850°C:

2Cr(OH)₃ → Cr₂O₃ + 3H₂O.

Alongside the main process of calcination, a part of the produced chromium oxide reacts with alkali thus forming sodium chromates which after calcination are again washed off, then dried and crushed.

To obtain pigment with a yellowish tinge, it is necessary that the chromium hydroxide III paste contain about 5% sodium hydroxide, with the calcination process performed at 780 to 800°C. To obtain a pigment with a bluish tinge, it is necessary that the chromium hydroxide III paste contain about 3% solution of boric acid, with the calcination process performed at 970-1000°C.

Viridian is chromium hydroxide III Cr₂O₃·nH₂O, with n = 1.5…2.5. This pigment is obtained by means of either the thermal method or the sedimentation method from sodium dichromate solutions. The first method [11] which has gained wider application, consists in calcination of mixture of boric acid and sodium or potassium dichromate at 550 to 600°C (7-10):

4H₃BO₃ → H₃B₂O₄ + 5H₂O;

K₂Cr₂O₇ + H₂B₄O₇ → K₂B₂O₇ + H₂Cr₂O₇;

2H₂Cr₂O₇ + 2H₂O → 2Cr₂O₃·2H₂O + 3O₂;

Cr₂O₇²⁻·2H₂O + H₂B₄O₇ → Cr₂O₃·2H₂O + 2B₂O₃ + 2H₂O.

Fusion cake obtained after calcination is treated with boiling water, with potassium pyroborate transiting into the solution and viridian remaining in the sediment. The sediment is washed off with hot water until almost complete removal of boric acid, then filtered, dried and crushed.

The second method of obtaining viridian consists of reducing concentrated solutions of chromates and sodium dichromate with organic compounds or hydrogen [12,13]. The process is performed at 350 to 360°C and a pressure of 35 MPa in a continuous processing plant.

Cobalt green is a solid solution of cobalt oxide in zinc oxide CoO·nZnO, with n = 15…50. The pigment’s colour changes from light green to dark green with the percentage of zinc oxide - the higher the percentage, the lighter the pigment. The pigment is obtained by means of calcination of easily dissociating cobalt salts mixed with zinc white at 1000 to 1100°C. Zinc white is stirred with a small amount of water, and then cobalt sulphate solution is added. During the mixing process, basic salts of the (OH)₂·CoSO₄ type are formed. The resulting paste is dried, crushed and calcined (11, 12).

Zn(OH)₂·CoSO₄ → ZnO + SO₃ + H₂O;

CoO + nZnO → CoO·nZnO.

The calcination product is crushed, washed, dried and finally re-crushed.

3. Synthesis of chromium-containing pigments from industrial wastes

Raw materials used for obtaining chromium pigments are trivalent or hexavalent chromium salts or sodium or potassium chromates (dichromates). The pigments are obtained by calcination of either chromic anhydride at a temperature of 1000°C or potassium or sodium dichromate with a reducing agent (sulphur, carbon) at 600 to 700°C depending on the obtained colour or various reagents treating raw materials [14].

It is possible to obtain green chromium-containing pigments from chromium-containing waste, viz. collected ferrochromium dust and dead catalysts [15-21].
Ferrochromium dust contains a relatively high percentage of chromium, iron, silicon and magnesium oxides. By using air and magnetic separation of the dust the percentage of chromium oxide raises to 70…75%, the percentage of iron - to 13…20% in the magnetic fraction. During the process of magnetic separation, silicon, aluminium and magnesium oxides almost completely transit into the non-magnetic fraction, thus making the non-magnetic fraction serve as an active admixture to cement. To obtain verditer green (chromium oxide) which meets the technical requirements, the magnetic fraction is treated with sulphuric acid while heating in a steam jacketed reactor or in an autoclave.

During the treatment, iron oxide reacts with sulphuric acid, thus forming a solution of ferrous sulphate, which is filtered off the sediment on a filter press. The chromium oxide paste forming on the filter’s surface is washed off water-soluble salts (ferrous sulphate), then is subjected to drying and crushing to the desired dimensions in a combined dryer and later is used for the production of various green-coloured paintwork materials.

While cooling on a vacuum crystallizer, the filtrate and the rinsing water form suspension of green vitriol, which later separates off green vitriol on a centrifuge.

4. Conclusions
The above-presented investigations allowed us to make the following conclusions:

1. A number of technologies for obtaining pigments of various composition and high quality with the use of high-performance equipment and new types of raw materials and industrial waste products has been developed.

2. The possibility of obtaining high quality pigments from fine dust formed at metallurgical and machine-building enterprises, has been confirmed.

3. An effective technology for obtaining pigments and fillers from wastes of natural ores by treating them with various reagents and with the use of high-performance equipment has been developed.

4. The optimum conditions of technological processes with application of higher productivity of equipment (autoclaves, dryers) have been specified, providing not only the increase of the raw material utilization factor, but also the improvement in pigment’s quality.

The implementation of advanced technologies for the processing of raw materials and industrial waste makes it possible to solve the problem of providing all industries with high-quality pigments.

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