CHROMIUM SULFATE TANNING POWDER

Chromium sulfate is the most important ingredient used in the tanning of leather, and hence is of great significance to New Zealand. It is manufactured from the simple reduction of Cr (VI) to Cr (III) by the addition of an excess of sulphur dioxide:

$$Na_2Cr_2O_7 + 3SO_2 + H_2O \rightarrow Cr_2(SO_4)_2(OH)_2 + Na_2SO_4$$

This reaction is carried out in a steam-heated vessel, and then the excess SO_2 is removed in a second reaction tower. Finally, the liquid product is spray-dried to form a powder which is then bagged and sold.

As dichromate is a highly poisonous compound, all emissions from the plant are closely monitored and all sump water is recycled and the chromium within it reused.

INTRODUCTION

In a country such as New Zealand, with an economy still largely based on agricultural activities, the tanning of hides and pelts from cattle and sheep is a major industry. This industry requires appreciable quantities of tanning chemicals in order to cater for an increasingly sophisticated market. The principal chemical used for tanning at the present time is basic chrome sulfate.

In 1976 a joint Company was formed, Chrome and Chemicals (NZ) Ltd, with the intention of manufacturing basic chrome sulfate in this country. Fernz Corporation Ltd holds the majority interest in the company, the other partner being British Chrome and Chemicals Ltd. Basic chrome sulfate is marketed under the trade name Tannachrome. The company's plant for the manufacture of basic chrome sulfate was commissioned at the New Plymouth works of Farmers Fertiliser Ltd in December of 1976, and this plant has sufficient manufacturing capacity for the whole of New Zealand's requirements, with reserve capacity which allows for exports principally to Australia. Since commissioning, the plant has been producing chrome tanning powders to the same high quality standards as those produced by British Chrome and Chemicals Ltd.

THE MANUFACTURING PROCESS

The production of basic chrome sulfate is based on the chemical reaction in which hexavalent chromium (ie. +6 oxidation state) in the form of sodium dichromate, is reduced to the trivalent state (+3) by sulfur dioxide.

Step 1 - Reduction of hexavalent chromium

Anhydrous sodium dichromate powder, imported from the UK plant of British Chrome and Chemicals Ltd, is reduced by 'burner gas' from the fertiliser company's Contact sulfuric acid plant. Burner gas contains about 9% sulfur dioxide. The sodium dichromate is dissolved in water to make a strong solution which is pumped continuously over reaction towers filled

with ceramic packings where it reacts with the sulfur dioxide bearing gas. Although the reaction is exothermic, steam injection is required to maintain the temperature and hence the reaction rate. The product is 100% reduced to the +3 oxidation state and has a basicity of 33%. The terminology is often confusing as this product is referred to as being 33% reduced.

The chemical reaction involved is:

$$Na_2Cr_2O_7 + 3SO_2 + H_2O \rightarrow Cr_2(SO_4)_2(OH)_2 + Na_2SO_4$$

This compound is still freely water soluble. The sodium sulfate shown on the right hand side of the equation is part of the product and is normally not separated, and merely remains as an inert diluent.

An excess of sulfur dioxide is required to ensure the chromium is fully reduced to the +3 oxidation state. A second reaction tower is used to remove the residual sulfur dioxide.

As well as the 33% basicity products, 42% and 50% basicity products are manufactured by the addition of soda ash solution. These products are 'masked' by the addition of sodium formate, which alters the characteristics of the tanned leather.

Step 2 - Drying the product

The viscous green liquid produced by the foregoing process is converted to a dry powder by means of a spray drier, very similar to those used on a large scale in this country for the production of milk powders. The spray drier at this installation is direct fired by Kapuni natural gas and the product is packed directly into 25 kg bags from a small hopper.

ENVIRONMENTAL IMPLICATIONS

As chromium, particularly in the hexavalent oxidation state, is a toxic material, considerable attention was paid at the design stage in minimising emissions, both liquid and gaseous, from the plant. Emissions of chromium from the plant stacks are monitored regularly, but are rarely at detectable levels. A condition of the plant's air discharge permit is a requirement to continuously monitor sulfur dioxide emissions from the scrubber tower stack. All wash water is collected in a sump and reused for dissolving sodium dichromate raw material.

Chrome and Chemicals is currently working towards ISO 9000 registration.

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