Recovery and utilization of wash water solids generated during ilmenite leaching operation

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The solid content in the spent wash water generated during leaching operations in chloride process for the production of TiO\textsubscript{2} pigment is not recovered and considered waste. A method is proposed for the recovery of the solids and enrichment of titanium values in these solids. The composition of the recovered and enriched solids is determined by atomic absorption spectroscopy and other analytical techniques. The samples are characterized using X-ray diffraction (XRD) and scanning electron microscope (SEM). The pigmentary qualities of the recovered material are studied in enamel paint formulations and compared against commercial rutile TiO\textsubscript{2} pigment. Partial replacement of the TiO\textsubscript{2} pigment with the recovered material has not made any significant impact on the various characteristics studied and approached the commercial rutile TiO\textsubscript{2} pigment standards. Also partial replacement realizes a TiO\textsubscript{2} saving in enamel paint formulations.

Keywords: Wash water, dispersion, reducing strength, calcined solids

Introduction

The process for commercial production of TiO\textsubscript{2} from titaniferous ores by the chloride route process includes a combination of operational steps to economically produce high quality synthetic rutile\textsuperscript{1-8}. In the Benelite process\textsuperscript{2}, the ore after being reduced to the divalent state is subsequently subjected to leaching operation with hydrochloric acid under optimal conditions for dissolution of undesired non-titaniferous values in the ore. The management of the spent liquor generated during the above process represents a major environmental issue although many studies are reported for the recovery of valuables from it\textsuperscript{9-15}. Pyrohydrolysis of the spent liquor for recovery of hydrochloric acid\textsuperscript{16-18} generates an impure iron oxide with no marketable outlets. The titanium-rich leached ore is further washed-off the acidic content with water and the resulting wash water contains undesirable solids. The nature being fine, these solids could not be used as feed material for subsequent production of titanium dioxide pigment or elsewhere. The solid fines are neither economical to recover in a useable manner and hence ultimately considered as waste product. The present study attempts to develop a waste remedial process for recovery and enrichment of titanium values from the wash water and its value addition. Detailed investigations are also carried out on the characterization of the recovered material and its utilization in enamel paint applications.

Materials and methods

Materials

Chemicals used in the experiments include wash water suspension and surface treated TiO\textsubscript{2} pigment from the TiO\textsubscript{2} commercial plant, acrylic resin (Paraloid A-101) from Indofil Chemical Company, Mumbai, India, alkyd resin (Replakyd 516) from Rishab Phenolics, Hyderabad, India, benzyl butyl phthalate from Nice Chemicals, Cochin, India, commercial grade toluene, xylene, methylethyl ketone and mineral turpentine oil, silicone oil from Reliance Chemicals, Mumbai, and ethylene glycol mono ethyl ether acetate from Swastik Oil Products, Navsari, India. Alkyd and acrylic paint were prepared from the calcined powder, 5% and 10% blends of the processed material with TiO\textsubscript{2} pigment and from commercial rutile TiO\textsubscript{2} pigment for comparative evaluation. The samples were labeled S-1 (calcined powder), S-2 (5% S-1 blend with TiO\textsubscript{2} pigment), S-3 (10% S-1 blend with TiO\textsubscript{2} pigment) and S-4 (commercial rutile TiO\textsubscript{2} pigment).

Apparatus and equipments

The chemical composition of the samples was determined using Atomic Absorption Spectrometer
(PinnAAcle 900 F, PerkinElmer). The aluminum reduction technique (ASTM test method D1354-76) was employed to analyze the TiO$_2$ content of the samples.

Optical properties, such as L$_*$ (brightness) and b$_*$ (color) of dry compressed TiO$_2$ samples were determined using color spectrometer (CIELab, BYK-Gardener). The specular reflection of incident light from the paint film or gloss was measured at 20° with Sheen Glossmaster. The degree of dispersion of the samples was determined by Hegman Gauge (ASTM test method D1210-96). Carbon content in the samples was analyzed with Carbon Analyzer (Leco C-200) while Sartorious MA100 gave the moisture content in the calcined sample. XRD measurements were performed using XRD diffractometer (Rigaku, Miniflex II) operating in Cu Kα radiation and investigation on the morphology of the samples was carried out using SEM (Joel 6300F).

**Methods**

The wash water suspension with a specific gravity of 1.015 was stirred thoroughly and filtered using a laboratory vacuum filter. The resultant filter cake was washed with distilled water in the filter until pH of the filter cake (20% w/v) reported 5 or above. The filter cake was further subjected to calcinations in a laboratory muffle furnace at a temperature around 850°C for 4 hrs and thus obtained calcined solids were powdered. Acrylic (13.2 % PVC) and alkyd (18.0 % PVC) enamel paints were prepared using the calcined solid material processed from the wash water solids by weighing the following ingredients into a 50 ml polyethylene vial. 40.0 g glass beads, 10.0 g of calcined powder, 53.8 g of master batch prepared (for acrylic enamel) / 40.0 g glass beads, 11.0 g of the calcined powder, 26.0 g of master batch prepared 1 g drier (for alkyd enamel) and grinded for 15 minutes on Red Devil shaking apparatus. Paint was also prepared out of commercially available rutile grade surface treated TiO$_2$ pigment and was set as the standard. The beads were allowed to settle for 5 min, and side-by-side draw downs of the paint samples were made on white art cards placed under vacuum. Sufficient amount of paint has been used to make the draw down to produce the desired film thickness. Similar exercise was carried out with 5% and 10% blends of the processed material with TiO$_2$ pigment for comparative evaluation. The draw down samples were air dried for 3 hrs on a flat draft-free, dust-free surface and were evaluated for vehicle brightness and color, reducing strength etc.

**Results and Discussion**

**Chemical composition**

The chemical composition of the filtered washed cake and calcined solids were evaluated using the techniques mentioned above and the results are tabulated in Table 1. It is clear from the table that the calcination of the wash water solids has enriched the TiO$_2$ content considerably to 91.30% from 58.2%. The wash water solid is found to contain significant amounts of iron. The analysis revealed that the rutile TiO$_2$ pigment taken for comparative evaluation is moderately surface treated with SiO$_2$ and Al$_2$O$_3$ (2.20 % SiO$_2$ and 2.40 % Al$_2$O$_3$) for enhancement of pigmentary characteristics.

**Morphology**

XRD patterns of S-1 and S-4 exhibited strong diffraction peaks at 27°, 36° and 54°, which are assigned to the rutile phase of TiO$_2$ according to the standard spectrum (JCPDS No. 88-1175). A weaker, broader diffraction peak at 27° and absence of other peaks were characteristic of the XRD pattern of the recovered material before calcination which demonstrate its amorphous nature. The morphology of commercial TiO$_2$ (S-4) and calcined solids (S-1) have been observed through SEM. Both samples exhibits regular spherical morphology and their aggregation in micron range though the particle size of S-1 was slightly finer.

**Performance in paints**

The performance of the four samples in white acrylic as well as gray alkyd paint media was studied and the results are discussed below:

**Vehicle brightness and tone**

Brightness and tone were measured from pigmented paint film with color spectrometer. While

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Wash water solid</th>
<th>Calcined solid</th>
<th>TiO$_2$ pigment</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>58.20</td>
<td>91.30</td>
<td>91.70</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>2.62</td>
<td>4.54</td>
<td>96 ppm</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>0.82</td>
<td>1.53</td>
<td>2.20</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>0.10</td>
<td>0.15</td>
<td>2.40</td>
</tr>
<tr>
<td>C</td>
<td>1.70</td>
<td>Nil</td>
<td>0.15</td>
</tr>
<tr>
<td>Moisture</td>
<td>35.50</td>
<td>0.55</td>
<td>0.45</td>
</tr>
</tbody>
</table>
defining color characteristics, the intensity of the light is measured when it reflects back from pigmented film in different wavelengths of visible light. The brighter is pigment, more it reflects back light. From L and b values, L describes brightness of a pigment as proportional value in scale 0.....100. Value 100 corresponds to ideal white and 0 corresponds to black coat. Value of +b means yellow vehicle color tone and –b means blue tone. The vehicle brightness and vehicle color (tone) are the brightness and color values in paint media and the same for the four samples under study are shown in Figure 1 and Figure 2 respectively. The samples showed the following trend in brightness and color respectively: S-4 (96.88) > S-2 (96.52) > S-3 (95.96) > S-1 (83.30); S-1 (16.82) > S-3 (0.81) > S-2 (0.58) > S-4 (0.52). S-4 exhibited much superior vehicle brightness and bluer color in comparison against S-1 in acrylic media. The brightness of paint film with S-1 is substantially lower than that of other three samples. The comparatively diminutive change in brightness, ΔL (0.26) and color Δb (< 0.06) for S-2 against S-4 indicate the proximity of S-2 to S-4. S-1 and S-2 exhibited very high and low variations in brightness/color values respectively against S-4. The low vehicle brightness and yellower vehicle color for S-1 albeit similar TiO₂ values for S-4 can be attributed to the presence of undesirable presence of iron in the processed material.

Reducing strength

Reducing strength is studied from a paint tinted to some color, often to gray with black paste. Reducing strength of white pigments means capability of pigment to whiten black or pigmented mixture. It is an indicator of the degree of pigment dispersion. The reducing strength values have exhibited similar trend as in the case of acrylic vehicle brightness. S-1 (43.6%) is found to be weaker by more than 50% against other three samples [S-2 (99.3), S-3 (98.5), S-4 (100)]. Likewise brightness, the strength of sample blended with 5% processed material (S-2) is very much comparable with S-4 indicating better dispersion. The reducing strength of S-3 is also found be comparable.

Gloss

Gloss is determined by measuring specular reflection of incident light coming in particular angle from the pigmented paint film. Typically, the gloss of a paint film decreases with an increase in the pigment aggregate size and surface roughness. The brightness of a pigment is due to diffuse reflection while the gloss is due to specular reflection. The specular reflection of incident light from the paint film was measured at angles of 20°. As represented in the values of gloss in Figure 3, S-4 (53.5) and S-2 (53.5) provided the highest paint gloss and hence the lowest pigment aggregation and surface roughness. No significant loss in gloss of S-4 is detected on blending 5% of S-1 and the paint gloss is found decreasing to a small extent beyond 5% blending.

Hegman gauge dispersion

The results of the Hegman Gauge dispersion studies confirm the findings of the vehicle brightness, reducing strength, and gloss experiments. The dispersion level of S-2 (6.75) was at par with commercial TiO₂ grade (6.75) and only a marginal reduction in the dispersion level is detected (6.50) for
The recovery, enrichment and utilization of the wash water solids realize a TiO₂ marginal extent. The recovery, enrichment and (upto 10%) affected the pigment dispersion only to a smooth and glossy surface. Blending in higher ratios characteristics in the dry paint film resulting in recovered material provided excellent dispersion. SEM confirmed the rutile phase and micron range water generated during leaching operations. XRD and enrichment of titanium values from the spent wash

Conclusion

A method was proposed for the recovery and enrichment of titanium values from the spent wash water generated during leaching operations. XRD and SEM confirmed the rutile phase and micron range particle size of the recovered material. The recovered material was assessed for optical properties in enamel paint media. The results provided a detailed and complementary picture of the dry film dispersion properties. It exhibited inferior optical properties as a result of presence of iron in considerable amounts. Blending commercial TiO₂ pigment with 5% recovered material provided excellent dispersion characteristics in the dry paint film resulting in smooth and glossy surface. Blending in higher ratios (upto 10%) affected the pigment dispersion only to a marginal extent. The recovery, enrichment and utilization of the wash water solids realize a TiO₂ saving by atleast 5% replacement in enamel paint formulations. There is a clear potential for cost savings associated with replacement of TiO₂ pigment with the recovered material which is presently not recovered and considered waste. The practical utility of current process requires further optimization of various parameters and also economic assessment of the process.

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