(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)
(19) World Intellectual Property Organization
International Bureau
(43) International Publication Date
4 October 2012 (04.10.2012)

(51) International Patent Classification:
C04B 2/04 (2006.01)
(21) International Application Number:
PCT/IB20 12/000872
(22) International Filing Date:
26 April 2012 (26.04.2012)
(25) Filing Language:
English
(26) Publication Language:
English
(30) Priority Data:
1105365.9 30 March 2011 (30.03.2011) GB
(71) Applicant (for all designated States except US): THE UNIVERSITY OF DUNDEE [GB/GB]; Nethergate, Dundee DDI 4HN (GB).
(72) Inventors:
NEWLANDS, Moray, David [GB/GB]; College of Art, Science and Engineering, The University of Dundee, Nethergate, Dundee DDI 4HN (GB).
CSHENYI, Laszlo, Jozsef [HU/GB]; College of Art, Science and Engineering, The University of Dundee, Nethergate, Dundee DDI 4HN (GB).
ZHENG, Li [GB/GB]; College of Art, Science and Engineering, The University of Dundee, Nethergate, Dundee DDI 4HN (GB).
(74) Agent: BLACK, Simon, John; Black and Associates Limited, 4 Woodside Place, Glasgow G3 7QF (GB).


Published:
— without international search report and to be republished upon receipt of that report (Rule 48.2(g))
— with information concerning request for restoration of the right of priority in respect of one or more priority claims; the decision of the receiving Office regarding the request for restoration is pending and will be published separately once available (Rules 26bis.3 and 48.2(f))

(54) Title: COLOURED CONSTRUCTION COMPOSITIONS

Figure 1. Particle size distribution of toners and Portland cement

(57) Abstract: A multi-component admixture containing a surfactant which is adapted to provide an interface between hydrophobic toner particles and a hydrophilic cement-based or gypsum-based mix such as concrete or plaster to facilitate homogeneous mixing of the two materials.
Coloured Construction Compositions

Introduction

This invention relates to coloured construction compositions and, in particular, to coloured cement- and gypsum- based compositions such as mortar, plaster, concrete and to an admixture for use in dispersing and suspending the colour in such compositions.

Background of the Invention

Coloured cement- and gypsum- based compositions such as mortar, plaster and concrete are widely used in construction. Coloured concrete in particular is used to produce roof tiles, paving slabs, internal flooring and work surfaces while coloured mortar is used both in external and internal works and coloured plaster can be used to achieve internal decorative finishes.

Three main methods are employed to colour concrete - integral colouring, dry shake colouring and surface-applied stains and coatings.

The application of stains and coatings to impart a colour to concrete is the least expensive colouring method. However, the coloured concrete can suffer from poor durability and re-application may be required over time. In the dry shake method, coloured compounds are applied to freshly laid concrete and finished manually to
create a coloured appearance. However, the finishing process is labour intensive and costly.

In integrally coloured concrete, expensive pigments are employed to colour the concrete. Accordingly, integrally coloured concrete has a high material cost but, as no finishing process is required, a lower labour expense. The pigments employed are hydrophilic inorganic mineral pigments such as iron oxides, chromium oxides and the like. The pigment is introduced into the concrete mix at manufacture in liquid or powder form and the resultant coloured concrete is employed in the usual way. Although integrally coloured concrete can be less susceptible to fading than concrete coloured using alternative methods, the finished product can nevertheless still be susceptible to surface damage, efflorescence, dirt and mould which can obscure the colour. The application of curing compounds or sealers can sometimes be necessary to protect the coloured surface thereby further increasing the cost.

In an industry totally unrelated to construction, the increasing demand for producing quality documents results in the world-wide use of a large amount of office consumables including toner cartridges. Toner powder is the fine dry ink used in laser printers, copiers and fax machines. Waste toner powder is derived from two main sources - sub-standard toner powder from the manufacturing process and the residue present in spent cartridges. Even where spent cartridges are recycled, the toner powder removed from spent cartridges is degraded and not suitable for re-use. Moreover, due to the fine nature of toner powder, handling presents a dusting hazard so that the only cost-effective disposal option is landfilling in closed containers.
Attempts have been made to find methods to recycle waste toner powder. For example, waste toner powder has been employed in the production of Black Masterbatch, a dye which can be used to colour polymers and is used in the manufacture of plastics products such as automotive parts, sheets and bags. However, heretofore, the hydrophobic nature of waste toner powder has severely limited its recycling potential.

In 2004, it was estimated that a minimum of 700 tonnes of waste toner powder was generated during toner manufacture in the United Kingdom alone while 300,000 tonnes of waste toner cartridges containing significant amounts of waste toner powder were landfilled.

**Summary of the Invention**

According to the invention there is provided a surfactant admixture for use in cement-based and gypsum-based construction compositions comprising an anionic surfactant, a non-ionic surfactant and water wherein the ratio of the non-ionic surfactant to the anionic surfactant is about 3:1 and the ratio of water to anionic surfactant is about 36:1.

Preferably, the anionic surfactant comprises sodium dodecyl benzene sulfonate and the non-ionic surfactant comprises polyethylene glycol terf-octylphenyl ether.

Advantageously, the water comprises distilled water.
The invention also extends to a pigment for colouring cement-based and gypsum-based construction compositions comprising a surfactant admixture as hereinbefore defined, a toner powder and water.

In a preferred embodiment of the invention, the toner powder comprises waste toner powder.

Preferably, the admixture is present in an amount up to 2% of toner powder, more preferably in an amount from about 0.20% to about 0.50% of toner powder and most preferably, in an amount from about 0.30% to about 0.35% of toner powder.

Preferably, the pigment comprises 40% toner powder.

In an alternative embodiment of the invention, the pigment is formed into a pellet, dough or paste.

The invention also extends to a construction composition comprising cement, water, an amount of toner powder effective to colour the construction composition and a surfactant admixture for dispersing the toner powder in the construction composition.

Preferably, the surfactant admixture comprises an anionic surfactant, a non-ionic surfactant and water wherein the ratio of the non-ionic surfactant to the anionic surfactant is about 3:1 and the ratio of water to anionic surfactant is about 36:1.
Preferably, the admixture is present in an amount up to 2% of toner powder, more preferably in an amount from about 0.20% to about 0.50% of toner powder and most preferably, in an amount from about 0.30% to about 0.35% of toner powder.

Suitably, the cement comprises Portland cement.

Advantageously, the construction composition further comprises an aggregate. Preferably, the aggregate is selected from the group comprising sand, gravel and stone. More preferably, the aggregate comprises sand and gravel to form a coloured concrete composition.

The invention also extends to a method for producing a coloured cement-based construction composition comprising mixing the cement with water, an amount of toner powder effective to colour the cement and a surfactant admixture for dispersing the toner powder in the construction composition.

Preferably, the toner powder comprises waste or spent toner powder.

Advantageously, the surfactant admixture comprises an anionic surfactant, a non-ionic surfactant and water wherein the ratio of the non-ionic surfactant to the anionic surfactant is about 3:1 and the ratio of water to anionic surfactant is about 36:1.

Preferably, the anionic surfactant comprises sodium dodecyl benzene sulfonate and the non-ionic surfactant comprises polyethylene glycol terf-octy lphenyl ether.
Suitably, the water comprises distilled water.

In yet a further embodiment, the invention also extends to the use of a surfactant admixture comprising an anionic surfactant, a non-ionic surfactant and water wherein the ratio of the non-ionic surfactant to the anionic surfactant is about 3:1 and the ratio of water to anionic surfactant is about 36:1 in the preparation of a coloured cement-based construction composition comprising a toner powder.

 Preferably, the toner powder comprises waste or spent toner powder.

 Advantageously, the anionic surfactant comprises sodium dodecyl benzene sulfonate and the non-ionic surfactant comprises polyethylene glycol fe/f-octylphenyl ether.

Suitably, the water comprises distilled water.

**Brief Description of the Drawings**

The invention will now be described, by way of example only, with reference to the accompanying drawings and non-limiting Examples in which:

Figure 1 illustrates the particle size distribution for the black toner, cyan toner, magenta toner and CEM I Portland cement employed in the Examples;
Figure 2 illustrates three scanning electron microscope images of the black toner, cyan toner and magenta toner of Figure 1;

Figure 3 illustrates the setting times of the 5%, 10% and 20% black toner cement paste mixtures in block diagram format;

Figure 4 illustrates the setting times of the 5%, 10% and 20% red/magenta toner cement paste mixtures in block diagram format;

Figure 5 illustrates the setting times of the 5%, 10% and 20% cyan/blue toner cement paste mixtures in block diagram format, and

Figure 6 illustrates photographs of the Portland Cement reference sample, the cement paste sample with 20% by weight black toner, the Cement Paste with 20% by weight magenta toner and Cement Paste with 20% by weight cyan toner in the leaching test with bubbles visible on the hydrophobic cement pastes containing toner.

**Detailed Description of the Invention**

Surprisingly, the applicant has found that hydrophobic waste toner powder can be recycled in an environmentally friendly manner by combining the hydrophobic waste toner powder with hydrophilic cement-based or gypsum-based compositions in a non-hazardous manner to produce improved, durable, integrally coloured cement-based or gypsum-based compositions such as plaster, mortar and concrete.
The hydrophobic waste toner is effectively dispersed and suspended for a sufficient period in the surfactant admixtures of the invention to render the resultant compositions suitable for use in plaster, mortar and concrete applications and the like.

Moreover, due to the pore blocking effect of the fine waste toner particles (about 10 μm in diameter) and their partially retained water repellent properties, concrete compositions of the invention exhibit improved water tightness to enhance durability and suppress efflorescence over time.

As described in the Examples, the coloured concrete products of the invention exhibit comparable or improved engineering and durability properties compared to non-coloured reference concrete products.

The present invention facilitates the use of a recycled product (waste toner powder) at a lower cost than known dedicated concrete pigments whilst reducing and/or avoiding surface treatment and maintenance. In addition, the compositions and methods of the invention result in a decorative concrete in one step without requiring modification of known mixing technology. Moreover, due to the desirable strength characteristics of the concrete products of the invention, the products are suitable for use in high strength applications such as building construction, railway sleepers and the like.
Current market share of coloured concrete is heavily influenced by the high product costs due to the costliness of the pigments employed - e.g. in the United Kingdom concrete pigments currently cost about from £2/kg to £5/kg, giving rise to additional costs from £30 to £707m$^3$ of concrete compared with costs from £40 to £70/m$^3$ for grey concrete.

The present invention therefore reduces the cost of coloured cement-based and concrete products whilst at the same time disposing of, re-cycling and exploiting what is otherwise a hazardous waste toner product.

**Multi-Component Admixture**

It has been found that a multi-component admixture in accordance with the invention is adapted to provide an interface between hydrophobic toner particles and a hydrophilic cement-based or gypsum-based mix such as concrete or plaster, respectively, to facilitate homogeneous mixing of the two materials. The admixture also functions as an anti-flocculant which prevents the hydrophobic waste toner powder from forming flocculates in the hydrophilic cement-based or gypsum-based mixture and facilitates mixing and dispersal of the waste toner powder in the cement-based or gypsum-based mixture.

The admixture is made up of a surfactant component having functional groups capable of binding apolaric matter such as waste toner powder. An admixture made up of a combination of an anionic and a non-ionic surfactant has been found to be particularly efficacious. A preferred anionic surfactant for use in the admixture is
dodecyl benzene sulfonic acid sodium salt (sodium dodecyl benzene sulfonate) - DBS, CAS Number 251 55-30-0. A preferred non-ionic surfactant for use in the admixture of the invention is polyethylene glycol terf-octylphenyl ether (TritonX-100 (Trade Mark), CAS Number 9002-93-1). Where the aforementioned surfactants are employed in the admixture, the polyethylene glycol feri-octylphenyl ether and the sodium dodecylbenzene sulfonate are employed in a ratio of about 3:1.

The surfactants are diluted in distilled water to form the admixture with a typical ratio of distilled water to the sodium dodecylbenzene sulfonate being about 36:1.

As shall be described more fully below in the Examples, the amount of admixture employed is dependent on the quantity of the waste toner powder employed to colour the cement-based composition. The required level of admixture was found to depend on the type of admixture and toner powder as well as on their target concentration in water. In general a dosage of admixture of up to about 2% by weight of the quantity of toner can be employed. However, a dosage of from about 0.20% to about 0.50% by weight and preferably from about 0.30% to 0.35% by weight of the quantity of toner has been found to be particularly efficacious. In the production of concrete, the admixture is mixed with the waste toner and water to produce a slurry containing about 40% toner. This slurry is then mixed with the rest of the components of concrete.

As indicated above, the inventive admixture is preferably used at a level expressed as being from about 0.30% by weight to about 0.35% by weight of toner as depending on how much toner is added to a cubic meter of concrete, the inventive
admixture content relative to the mixing water changes. Accordingly, it is preferable
to specify the inventive admixture content as a percentage of toner as this value will
remain the same. Accordingly, if a slurry of 40% toner is used as mixing water, the
optimum admixture content is 1.2-1.4% in such mixing water.

The incorporation of the waste toner powder into a slurry also facilitates re-cycling by
eliminating the dusting hazard. The waste toner slurry also facilitates ease of
handling and precise proportioning in use.

As will be appreciated by those skilled in the art, the admixture/toner slurry can also
be prepared in more concentrated (suspended in less water but with a maintained
admixture to toner ratio typically being maintained) or indeed dilute form, provided
the subsequent mixing procedure employed ensures homogenisation of all
components. For example, where the specified admixture content relative to toner is
maintained at from about 0.30% by weight to about 0.35% by weight as described
above, a composition containing 60% by weight toner results in a manageable non-
dusting earth-dry powder, a composition containing about 55% by weight toner
results in a plastic dough, whereas a composition containing about 50% toner results
in a paste. All forms avoid segregation during transportation and enable
homogeneous mixing with ease.

In short, the admixture/toner slurry can be formed into pellets, doughs, pastes or the
like for subsequent mixing with the cement-based compositions.
The required level of admixture is dependent on the type of admixture and toner powder and their target concentration in water. However, in order to optimise the proportion of admixture and introduce toner in a form avoiding dust formation, waste toner is first brought to a slurry (up to 40% by mass) with water containing from about 0.3% - 0.35% admixture.

An admixture as described above was employed in the following Examples.

**Examples**

In the following Examples, three different colour toner powders, black, cyan (blue) and magenta (red) were obtained from Moock Environmental Solutions Limited. The toner powders were characterised by particle size distribution and morphology (particle shape). In the following Examples, Triton X-100 and DBS produced by Acros Organics were used in the admixture of the invention.

**Particle Size Distribution**

A Malvern Mastersizer2000 analyser was used to determine the particle size distribution of the toner powders. The results are shown in Figure 1. As shown in the drawing, the test results indicated that all toners were of a very narrow particle size range, practically uniform size approximately 10 μm in diameter. Figure 2 shows scanning electron microscope images of the black toner, cyan toner and magenta toner of Figure 1. As shown in the drawing, the scanning electron electron microscope revealed that the black toner had spherical particles, whereas the cyan
and magenta toner particles were slightly angular, which is in line with differing flow characteristics observed for the dry materials.

Example 1 - Cement Paste

1A. Setting Time

Nine cement pastes were prepared incorporating black, magenta and cyan toner at levels of 5%, 10% and 20% by weight cement. The cement pastes were mixed manually in a porcelain bowl using a spoon as described in BS EN 196-3 (Methods of Testing Cement - Part 3: Determination of Setting Times and Soundness).

The mix proportions and test results are indicated in Table 1 below:

<table>
<thead>
<tr>
<th>Mix</th>
<th>Mix proportions, gram/batch</th>
<th>Admixture (1.0% of toner)</th>
<th>Water requirement, % by mass</th>
<th>Setting time, hh:mm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PC</td>
<td>Toner</td>
<td>Water</td>
<td></td>
</tr>
<tr>
<td>PC ref.</td>
<td>500</td>
<td>0</td>
<td>140</td>
<td>0</td>
</tr>
<tr>
<td>5% black</td>
<td>475</td>
<td>25</td>
<td>145</td>
<td>0.25</td>
</tr>
<tr>
<td>10% black</td>
<td>450</td>
<td>50</td>
<td>125</td>
<td>0.50</td>
</tr>
<tr>
<td>20% black</td>
<td>400</td>
<td>100</td>
<td>175</td>
<td>1.0</td>
</tr>
<tr>
<td>5% magenta</td>
<td>475</td>
<td>25</td>
<td>145</td>
<td>0.25</td>
</tr>
<tr>
<td>10% magenta</td>
<td>450</td>
<td>50</td>
<td>125</td>
<td>0.50</td>
</tr>
<tr>
<td>20% magenta</td>
<td>400</td>
<td>100</td>
<td>175</td>
<td>1.0</td>
</tr>
<tr>
<td>5% cyan</td>
<td>475</td>
<td>25</td>
<td>145</td>
<td>0.25</td>
</tr>
<tr>
<td>10% cyan</td>
<td>450</td>
<td>50</td>
<td>160</td>
<td>0.50</td>
</tr>
<tr>
<td>20% cyan</td>
<td>400</td>
<td>100</td>
<td>180</td>
<td>1.0</td>
</tr>
</tbody>
</table>

The setting times are illustrated in block diagram format in Figures 3 to 5. As shown in the drawings, the water content required for standard consistency increased with increasing toner content and the setting times also increased. However, all results
were within the range of standard requirement (BS EN 197-1: Initial setting time \( \geq 60 \) min. ASTM C150-00: Initial setting time \( > 60 \) min and Final setting time \( < 600 \) min).

1B. **Leaching Test**

Toner levels tested were 0 (PC (Portland Cement) reference) 5%, 10%, 20% by mass cement in the specimens used for the Setting Time test outlined in Example 1A above.

Samples were placed in 120 mm cubic containers and 1000 ml distilled, deionised water was used as leachant. A 20 mm spacer was used to make sure each sample was located in the centre of the water bath and all spaces between the samples and the walls and bottom of the container and top water surface were larger than 20 mm.

- **pH value**

The pH value results are indicated in Table 2 below. By or soon after 3 days exposure to water, the pH values of the water for all samples reached about 12.5 which is the value of saturated \( \text{Ca(OH)}_2 \) solution at 25°C, indicating that an equilibrium had been established. The toner containing samples required more time than the PC reference sample to reach the saturated pH value as shown in the Table. Although the Applicants do not wish to be bound by any theorem, it is believed that the migration process of ions from the samples was hindered by the addition of toner. Accordingly, cement paste mixes of the invention are less likely to be affected by efflorescence.
Moreover, as shown in Figure 6, when the hardened paste samples of the invention were placed in leach water, a number of bubbles appeared on the surface of the cement pastes of the invention which indicated that the surface had become hydrophobic due to the addition of the toner powder so that water permeation and ion diffusion processes were suppressed when compared with cement pastes containing Portland Cement alone.

<table>
<thead>
<tr>
<th>Mix</th>
<th>pH value at various ages</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>start</td>
</tr>
<tr>
<td>PC</td>
<td>7.3</td>
</tr>
<tr>
<td>5% black</td>
<td>7.5</td>
</tr>
<tr>
<td>10% black</td>
<td>7.4</td>
</tr>
<tr>
<td>20% black</td>
<td>7.6</td>
</tr>
<tr>
<td>5% magenta</td>
<td>7.6</td>
</tr>
<tr>
<td>10% magenta</td>
<td>7.6</td>
</tr>
<tr>
<td>20% magenta</td>
<td>7.5</td>
</tr>
<tr>
<td>5% cyan</td>
<td>7.5</td>
</tr>
<tr>
<td>10% cyan</td>
<td>7.6</td>
</tr>
<tr>
<td>20% cyan</td>
<td>7.6</td>
</tr>
</tbody>
</table>
- **Other Leachates**

A colorimeter (Fisher Model 45) was used to measure all solutions to identify any discolouration of the leachate solutions. No change in colour was measured for all solutions in 2 weeks thereby indicating that the release of toner material was negligible i.e. less than 1.5 ppm over the period of the test. Follow up tests were also carried out after 6 months showing no further release.

**1B. Surface Colour Test**

A Minolta chroma meter (Model CR-210) was used to measure the surface colour of the Cement Paste samples of the invention prepared as described above. The results were also compared to the pure cyan, magenta, yellow and black colour prints from a LASER colour printer (Model Lexmark (Trade Mark) C522N) in accordance with the CIELAB colour definition system developed in 1976 by the Commission Internationale de l'Eclairage (International Committee on Illumination): Publication CIE 15.2-1986, Second Edition, CIE Recommendations on Colorimetry - BS ISO 12640-3:2007 Graphic technology; Prepress digital data exchange, CIELAB standard colour image data (CIELAB/SCID).

The values were expressed with the L\(^*\)a\(^*\)b\(^*\) colour system, in which L\(^*\) is the lightness factor, a\(^*\) and b\(^*\) are the chromaticity coordinates for "red-green" and "blue-yellow" respectively.
The results are summarised in Table 3 below:

**Table 3**

Chromatic values in L a b' colour space

<table>
<thead>
<tr>
<th>Toner</th>
<th>L: Contrast</th>
<th>a: Red(+), Green(-)</th>
<th>b: Yellow(+), Blue(-)</th>
<th>L: Contrast</th>
<th>a: Red(+), Green(-)</th>
<th>b: Yellow(+), Blue(-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC reference</td>
<td>58.76</td>
<td>3.13</td>
<td>39.29</td>
<td>-0.73</td>
<td>1.34</td>
<td></td>
</tr>
<tr>
<td>5% black</td>
<td>51.48</td>
<td>-0.17</td>
<td>1.78</td>
<td>50.63</td>
<td>-0.27</td>
<td>0.04</td>
</tr>
<tr>
<td>10% black</td>
<td>49.72</td>
<td>-0.42</td>
<td>-0.38</td>
<td>47.17</td>
<td>-0.32</td>
<td>-1.00</td>
</tr>
<tr>
<td>20% black</td>
<td>41.52</td>
<td>-0.23</td>
<td>-1.35</td>
<td>39.82</td>
<td>-0.39</td>
<td>-0.28</td>
</tr>
<tr>
<td>5% magenta</td>
<td>54.05</td>
<td>10.26</td>
<td>-2.12</td>
<td>50.91</td>
<td>8.46</td>
<td>-1.85</td>
</tr>
<tr>
<td>10% magenta</td>
<td>53.19</td>
<td>13.27</td>
<td>-2.77</td>
<td>47.27</td>
<td>12.23</td>
<td>-2.28</td>
</tr>
<tr>
<td>20% magenta</td>
<td>43.69</td>
<td>20.45</td>
<td>-1.80</td>
<td>47.11</td>
<td>19.79</td>
<td>-4.04</td>
</tr>
<tr>
<td>5% cyan</td>
<td>60.09</td>
<td>-5.44</td>
<td>-8.71</td>
<td>47.98</td>
<td>-3.18</td>
<td>-5.64</td>
</tr>
<tr>
<td>10% cyan</td>
<td>55.71</td>
<td>-4.42</td>
<td>-12.73</td>
<td>46.47</td>
<td>-3.88</td>
<td>-10.44</td>
</tr>
<tr>
<td>20% cyan</td>
<td>47.05</td>
<td>-4.47</td>
<td>-16.63</td>
<td>47.18</td>
<td>-3.82</td>
<td>-17.11</td>
</tr>
</tbody>
</table>

As can be seen from Table 3, increasing toner addition systematically changed the respective colour coordinates and contrast (lightness) values. Moreover, Table 3 demonstrates that toner can be homogeneously and stably incorporated in concrete, mortar and plaster in accordance with the invention with the proportions and overall quantity of various colour toners governing the colour of the product. A particular desired colour can also be achieved by adjusting and ascertaining by trial the applicable toner proportions in widely available colour charts.
Example 2 - Concrete

Concrete mixtures were made in a drum mixer with 0 (reference) 15% and 30% toner powder contents relative to cement content as shown in Table 4 below. Mixtures were also prepared and strength tested as outlined in Table 5 below. All aggregates and sand employed were in saturated surface dry condition. Toner was used as slurry, prepared using the half of the mixing water. The overall admixture content was 1% of mixing water which falls into the preferred range of 0.30% to 0.35% by weight toner as previously described. The same 1% admixture level was used in the mixing water when 15% and 0% toner was applied in order to have comparable samples which only differ from each other in their toner content.

<table>
<thead>
<tr>
<th>Toner content, %</th>
<th>Water, kg/m³</th>
<th>CEM I, kg/m³</th>
<th>Toner, kg/m³</th>
<th>Sand, kg/m³</th>
<th>Gravel, kg/m³</th>
<th>W/(C+T)</th>
<th>S/A</th>
<th>T/(C+T)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10 mm</td>
<td>20 mm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>175</td>
<td>350</td>
<td>0</td>
<td>610</td>
<td>375</td>
<td>750</td>
<td>0.50</td>
<td>0.35</td>
</tr>
<tr>
<td>15</td>
<td>175</td>
<td>297.5</td>
<td>52.5</td>
<td>600</td>
<td>370</td>
<td>735</td>
<td>0.50</td>
<td>0.35</td>
</tr>
<tr>
<td>30</td>
<td>175</td>
<td>245</td>
<td>105</td>
<td>600</td>
<td>370</td>
<td>735</td>
<td>0.50</td>
<td>0.35</td>
</tr>
</tbody>
</table>

Table 5

Concrete Mixtures with All Toners and White Cement for Strength Testing

<table>
<thead>
<tr>
<th>Colour</th>
<th>Water kg/m³</th>
<th>CEM I, kg/m³</th>
<th>Toner, kg/m³</th>
<th>Sand, kg/m³</th>
<th>Gravel, kg/m³</th>
<th>W/(C+T)</th>
<th>T/(C+T)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10 mm</td>
<td>20 mm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>White</td>
<td>175</td>
<td>350</td>
<td>0</td>
<td>600</td>
<td>1105</td>
<td>0</td>
<td>0.50</td>
</tr>
<tr>
<td>Yellow</td>
<td>200</td>
<td>245</td>
<td>105</td>
<td>600</td>
<td>1105</td>
<td>0</td>
<td>0.57</td>
</tr>
<tr>
<td>Cyan</td>
<td>188</td>
<td>245</td>
<td>105</td>
<td>600</td>
<td>1105</td>
<td>0</td>
<td>0.54</td>
</tr>
<tr>
<td>Magenta</td>
<td>200</td>
<td>245</td>
<td>105</td>
<td>600</td>
<td>1105</td>
<td>0</td>
<td>0.57</td>
</tr>
<tr>
<td>Black</td>
<td>188</td>
<td>245</td>
<td>105</td>
<td>600</td>
<td>1105</td>
<td>0</td>
<td>0.54</td>
</tr>
</tbody>
</table>
The following tests were performed on the above concrete mixtures:

- Strength development at 7 and 28 days (BS EN 12390-3:2009)
- Water penetration, 28 days (BS EN 12390-8:2009)
- Initial Surface Absorption Test (BS 1881-208:1996)
- Absorption, 28 days (BS 1217: 2008)

The test results are given in Tables 6 and 7 below.

**Table 6**
Concrete Test Results Employing Cyan Toner

<table>
<thead>
<tr>
<th>Toner content, %</th>
<th>Slump, mm</th>
<th>Compressive strength, N/mm²</th>
<th>Water penetration under pressure, mm</th>
<th>ISAT*, ml/(m²s)</th>
<th>Capillary absorption** mg/mm²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>7 days</td>
<td>28 days</td>
<td>10 min</td>
<td>30 min</td>
</tr>
<tr>
<td>0</td>
<td>15</td>
<td>37.9</td>
<td>46.5</td>
<td>0.381</td>
<td>0.253</td>
</tr>
<tr>
<td>15</td>
<td>25</td>
<td>28.7</td>
<td>35.4</td>
<td>0.332</td>
<td>0.152</td>
</tr>
<tr>
<td>30</td>
<td>45</td>
<td>17.9</td>
<td>21.3</td>
<td>0.180</td>
<td>0.104</td>
</tr>
</tbody>
</table>

**Table 7**
Concrete Compressive Strength Test Results Employing All Toners

<table>
<thead>
<tr>
<th>Toner at 30% of cement</th>
<th>Slump, mm</th>
<th>Compressive strength, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>7 days</td>
</tr>
<tr>
<td>Ref. (white cement)</td>
<td>70</td>
<td>26.0</td>
</tr>
<tr>
<td>Yellow</td>
<td>90</td>
<td>18.0</td>
</tr>
<tr>
<td>Cyan</td>
<td>75</td>
<td>22.5</td>
</tr>
<tr>
<td>Magenta</td>
<td>78</td>
<td>19.0</td>
</tr>
<tr>
<td>Black</td>
<td>80</td>
<td>21.0</td>
</tr>
</tbody>
</table>
As shown above, with increased addition of toner at the expense of Portland cement, concrete strength values decreased - in particular as shown above with concrete made with white cement although the strength improvement is obtained with both grey and white concrete. However, the decrease was not as pronounced as that observed for an equivalent cement replacement level, indicating a net strength improvement.

For example, where the applied level was 30% toner of cement at the expense of Cement (Table 5), 70% of strength is expected from concrete with 70% of cement of the reference i.e. $0.7 \times 40.0 \text{ MPa} = 28.0 \text{ MPa}$ which is met or exceeded by the toner containing test concretes of the invention.

It should be noted that slump is the reduction of height of a 300 mm cone of fresh concrete when removed from its metal sleeve. The higher the water content, the higher the slump. However, if the water content is high, the resulting concrete has more pores in place of the extra water and consequently lower strength.

With suitable modifications of the mix design, compressive strength similar to that of control concrete is thought to be achievable with some savings of cement, due to pore blocking/improved packing effect due to the presence of toner particles.

The water absorption tests revealed that ingress of moisture into the concrete of the invention reduced at atmospheric pressure due to the water repellent and pore blocking properties of the toner.

The slight increase of water penetration under pressure shows the detrimental effect
of lack of cement, similarly to compressive strength results.

BS 1217:2008 prescribes that the ISAT values obtained shall not exceed 0.25 ml/(m²·s) at 10 minutes. This was achieved with 30% toner addition. However, it is believed that desirable ISAT levels can also be achieved with other toner concentrations by adjusting water and fine aggregate contents within the scope of the invention. Nevertheless, the reference concrete is the worst performer with increasing toner addition clearly reducing absorption.

Indeed, the 15% toner sample is close to the ISAT sample and it is believed that a level of about 16-17% toner would be the acceptable for this particular concrete mix. However, as indicated above, adjustment of other concrete components (e.g. water or fine aggregate contents) will result in acceptable toner levels of even less than 15%.

The invention is not limited to the embodiments herein described which may be varied in construction and detail without departing from the scope of the invention.
Claims

1. A surfactant admixture for use in cement-based and gypsum-based construction compositions comprising an anionic surfactant, a non-ionic surfactant and water wherein the ratio of the non-ionic surfactant to the anionic surfactant is about 3:1 and the ratio of water to anionic surfactant is about 36:1.

2. A surfactant admixture as claimed in Claim 1 wherein the anionic surfactant comprises sodium dodecyl benzene sulfonate.

3. A surfactant admixture as claimed in Claim 1 or Claim 2 wherein the non-ionic surfactant comprises polyethylene glycol ferr-octylphenyl ether.

4. A surfactant admixture as claimed in any of Claims 1 to 3 wherein the water comprises distilled water.

5. A pigment for colouring cement-based and gypsum-based construction compositions comprising a surfactant admixture as claimed in any of Claims 1 to 4, a toner powder and water.

6. A pigment as claimed in Claim 5 wherein the toner powder comprises waste toner powder.

7. A pigment as claimed in Claim 5 or Claim 6 wherein the admixture is present in an amount up to 2% of toner powder.
8. A pigment as claimed in any of Claims 5 to 7 wherein the admixture is present in an amount from about 0.20% to about 0.50% of toner powder.

9. A pigment as claimed in any of Claims 5 to 8 wherein the admixture is present in an amount from about 0.30% to about 0.35% of toner powder.

10. A pigment as claimed in any of Claims 5 to 9 comprising 40% toner powder.

11. A pigment as claimed in any of Claims 5 to 10 wherein the pigment is formed into a pellet, dough or paste.

12. A construction composition comprising cement, water, an amount of toner powder effective to colour the construction composition and a surfactant admixture for dispersing the toner powder in the construction composition.

13. A construction composition as claimed in Claim 12 wherein the surfactant admixture comprises an anionic surfactant, a non-ionic surfactant and water wherein the ratio of the non-ionic surfactant to the anionic surfactant is about 3:1 and the ratio of water to anionic surfactant is about 36:1.

14. A construction composition as claimed in Claim 12 or Claim 13 wherein the admixture is present in an amount up to 2% of toner powder.
15. A construction composition as claimed in any of Claims 12 to 14 wherein the admixture is present in an amount from about 0.20% to about 0.50% of toner powder.

16. A construction composition as claimed in any of Claims 12 to 15 wherein the admixture is present in an amount from about 0.3% to 0.35% toner powder.

17. A construction composition as claimed in any of Claims 12 to 16 wherein the cement comprises Portland cement.

18. A construction composition as claimed in any of Claims 12 to 17 further comprising an aggregate.

19. A construction composition as claimed in Claim 18 wherein the aggregate is selected from the group comprising sand, gravel and stone.

20. A construction composition as claimed in Claim 19 wherein the aggregate comprises sand and gravel to form a coloured concrete composition.

21. A method for producing a coloured cement-based construction composition comprising mixing the cement with water, an amount of toner powder effective to colour the cement and a surfactant admixture for dispersing the toner powder in the construction composition.
22. A method as claimed in Claim 21 wherein the toner powder comprises waste or spent toner powder.

23. A method as claimed in Claim 21 or Claim 22 wherein the surfactant admixture comprises an anionic surfactant, a non-ionic surfactant and water wherein the ratio of the non-ionic surfactant to the anionic surfactant is about 3:1 and the ratio of water to anionic surfactant is about 36:1.

24. A method as claimed in Claim 23 wherein the anionic surfactant comprises sodium dodecyl benzene sulfonate.

25. A method as claimed in Claim 23 or Claim 24 wherein the non-ionic surfactant comprises polyethylene glycol fett-octylphenyl ether.

26. A method as claimed in any of Claims 23 to 25 wherein the water comprises distilled water.

27. Use of a surfactant admixture comprising an anionic surfactant, a non-ionic surfactant and water wherein the ratio of the non-ionic surfactant to the anionic surfactant is about 3:1 and the ratio of water to anionic surfactant is about 36:1 in the preparation of a coloured cement-based construction composition comprising a toner powder.

28. Use as claimed in Claim 27 wherein the toner powder comprises waste or spent toner powder.
29. Use as claimed in Claim 27 or 28 wherein the anionic surfactant comprises sodium dodecyl benzene sulfonate.

30. Use as claimed in any of Claims 27 to 29 wherein the non-ionic surfactant comprises polyethylene glycol te/octylphenyl ether.

31. Use as claimed in any of Claims 27 to 30 wherein the water comprises distilled water.

32. A surfactant admixture substantially as hereinbefore described with reference to the Examples.

33. A pigment for colouring cement-based construction compositions substantially as hereinbefore described with reference to the Examples and/or as shown in the accompanying drawings.

34. A construction composition substantially as hereinbefore described with reference to the Examples and/or as shown in the accompanying drawings.

35. A method for producing a coloured cement-based construction composition substantially as hereinbefore described with reference to the Examples.

36. Use of a surfactant admixture substantially as hereinbefore described with reference to the Examples.
Figure 1. Particle size distribution of toners and Portland cement