In the practice of this invention, the term "substantially dry" denotes a flowable particulate apparently dry solid containing up to 12 to 16% moisture and preferably 12½% to 13½% moisture.

The dissociation constants indicated above are determined at the conditions most generally accepted in the literature for determinations of this kind. These conditions are a temperature of from 20 to 30 degrees C., and anionic strength of 0.1, using an electrolyte consisting of potassium chloride.

It is to be understood that these conditions of measurement are not those encountered during the washing, but represent a standard for indicating and determining the appropriate dissociation constants which will enable the skilled worker to choose the desired sequestering agents for the detergent compositions of this invention. In this regard, it should be noted that the optimum concentration of copper ions beyond which the speed of decomposition of the perborate, which increases with the concentration of copper ions, becomes too rapid for good bleaching effect.

Slight changes in the concentration of copper ions below or above optimum (which is about 0.00001 to 0.0001 molar) will result in a decrease in the bleaching power of the perborate. In practice it was heretofore impossible to obtain this optimum concentration. However, the sequestering agents essential for the compositions of this invention form a metal buffer with the water-soluble copper salt, which maintains the amount of free copper present in the washing medium at a value corresponding to that conducive to maximum bleaching efficiency irrespective of copper additions which are far in excess of that necessary to achieve that maximum value.

The selection of an organic detergent for use in the compositions of the present invention is not narrowly critical. The detergent may be any water-soluble anionic, or non-ionic compound having detergent properties. Examples of suitable anionic detergents which fall within the scope of the invention include the soaps, such as the water-soluble salts of higher fatty acids or rosin acids such as may be derived from fats, oils and waxes of animal, vegetable or marine origin, e.g. the sodium soaps of tallow, grease, coconut oil, tall oil and mixtures thereof; and the sulfated and sulfonated synthetic detergents, particularly those having about 8 to 26 and preferably about 12 to 22 carbon atoms to the molecule.

As examples of suitable synthetic anionic detergents there may be cited the higher alkyl mononuclear aromatic sulfonates such as the higher alkyl benzene sulfonates containing from 10 to 16 carbon atoms in the alkyl group, (e.g. the sodium salts of tetrapropyl, hexyl, octyl, nonyl, decyl, dodecyl or keryl benzene sulfonates) and the higher alkyl toluenes, xylene and phenol sulfonates; alkyl naphthalene sulfonates, such as sodium di-isopropyl naphthalene sulfonate, amine sodium naphthalene sulfonate, and sodium dinonyl naphthalene sulfonate; sulfated aliphatic alcohols such as sodium dodecyl and hexadecyl sulfates, triethanolamine dodecyl sulfate, and sodium oleyl sulfate; sulfated and sulfonated fatty oils, acids or esters, such as the sodium salts of sulfonated castor oil and sulfated red oil; sulfated hydroxyamides such as sulfated hydroxyethyl lauramide; sodium salt of lauryl sulfosuccinate; sodium salt of dioctyl sulfosuccinate; and the sodium salt of oleyl methyl tauride.

Also included within the scope of the invention are the sulfuric acid esters of polyhydric alcohols incompletely esterified with higher fatty acids, e.g. coconut oil monoglyceride monosulfate, tallow diglyceride monosulfate; and the hydroxy sulfonated higher fatty acid esters such as the higher fatty acid esters of low molecular weight alkyl sulfonic acids, e.g. oleic acid ester of thiosalic acid.
In order to obtain the best results, the amount of copper salt in the detergent composition of this invention must be such that the composition contains from about 30 to about 300 p.p.m. (parts per million) of copper and preferably from 40 to 80 p.p.m. The associated amount of sequestering agent should be such that about 3 to 15 molecules and preferably 10 to 13, thereof, should be present per atom of copper in the detergent composition. The composition of this invention can be prepared in any suitable manner such as, e.g., by spray drying the detergent mixture, the mineral salts, and the copper salt, and then adding, by dry mixing, the perborate and the sequestering agent as well as those constituents which could be sensitive to heat, such as perfume.

The bleaching efficiency percentage of the compositions of this invention is determined as follows:

Samples of cotton fabric are dyed by means of an oxidizable dye and washed with a bleach-free organic detergent until the complete removal of the excess of dye. These dyed fabrics, having a reflectance on a Hunter colorimeter in the range of 20, are washed with a detergent composition containing an organic detergent and a persalt, in glass beakers, for the time intervals and at temperatures used in a normal washing at the boil. The persalt partly oxidizes the dye and after washing, the fabric is lighter than at the start.

The reflectance of the fabric is measured by means of a Hunter photocolorimeter equipped with a green filter. For convenience the reflectance may be represented as BD before dyeing, BW before washing, and AW after washing. The bleaching efficiency, in percent, is then 100 (AW-BW) divided by (BD-BW).

The following formulations are representative of the compositions of this invention:

Water-soluble organic anionic or nonionic detergent (Synthetic detergent, soap or their mixtures) 4 to 40%.
Water-soluble inorganic salts 40 to 90%.
Perborate, especially sodium 3 to 20%.
Water-soluble copper salt in an amount corresponding in relation to the entire composition of 30 to 300 p.p.m. of Cu (.003% to .03%).

Sequestering agent which forms a copper complex having a dissociation constant the common logarithm of which is between -11 and -15, in an amount corresponding for each atom of Cu, of 3 to 15 molecules.
Perfume, coloring matter, blueing agent 0 to 1%.

The following examples are given further to illustrate the invention. They are not to be regarded as limiting, the claims being the sole limitation. All amounts and percentages in the specification and in the examples are by weight unless otherwise indicated.

**EXAMPLE 1**

A "basic" detergent composition is made of the following formulation:

<table>
<thead>
<tr>
<th>Percent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium dodecylbenzene sulfonate</td>
</tr>
<tr>
<td>Sodium tripolyphosphate</td>
</tr>
<tr>
<td>Monoethanolamide of coconut oil fatty acid</td>
</tr>
<tr>
<td>Sodium silicate</td>
</tr>
<tr>
<td>Magnesium silicate</td>
</tr>
<tr>
<td>Hydrated sodium perborate</td>
</tr>
<tr>
<td>Fluorescent dye, perfume, sodium sulfate, and moisture, balance to</td>
</tr>
</tbody>
</table>
Washing solutions are prepared by dissolving 12.5 grams or 5 grams per liter of the above basic detergent composition in aqueous washing mediums. Washing is then carried out at the boil and the results noted using each solution. Other washing solutions are prepared in like manner but with the difference that methylaminodiacetic acid, hydroxyethylaminodiacetic acid or aminotriacetic acid sequestrants are separately added to the basic detergent compositions at concentrations of 0.2% by weight of the basic detergent composition.

To separate portions of the respective washing solutions 0, 1, 2, 3, 4 or 5 p.p.m. of copper ions are added, in the form of copper sulfate, and washing is thereupon carried out. The obtained results are indicated in Table I below. In this table maximum bleaching attained for each of the formulas is indicated as well as the length of the bleaching "plateau." This "plateau" is defined as the interval of concentrations in copper ions (as p.p.m. in the washing solution) for which the maximum bleaching efficiency is not reduced by more than 10% of the maximum value.

### Table I

<table>
<thead>
<tr>
<th>Sequestering agent</th>
<th>8. g/l. of detergent composition</th>
<th>12.5 g/l. of detergent composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Maximum bleaching efficiency, percent</td>
<td>Length of bleaching &quot;plateau&quot;</td>
</tr>
<tr>
<td>None</td>
<td>100</td>
<td>80</td>
</tr>
<tr>
<td>Methylaminodiacetic acid</td>
<td>11.1</td>
<td>56</td>
</tr>
<tr>
<td>Sodium dodecylbenzene sulfonate</td>
<td>8.5</td>
<td>48</td>
</tr>
<tr>
<td>Sodium salt of sulfated lauryl alcohol</td>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>Monoethanolamide of coconut oil fatty acid</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>Sodium tripolyphosphate</td>
<td>40</td>
<td>0.5</td>
</tr>
<tr>
<td>Sodium silicate</td>
<td>7.0</td>
<td>0.75</td>
</tr>
<tr>
<td>Sodium perborate tetrahydrate</td>
<td>10.0</td>
<td>3.8</td>
</tr>
<tr>
<td>Copper acetate in an amount corresponding in relation to the entire composition of 80 p.p.m. of Cu.</td>
<td>10.0</td>
<td>3.8</td>
</tr>
<tr>
<td>Hydroxyethylaminodiacetic acid</td>
<td>4.7</td>
<td>4.7</td>
</tr>
<tr>
<td>Aminotriacetic acid</td>
<td>4.7</td>
<td>4.7</td>
</tr>
</tbody>
</table>

### Table II

<table>
<thead>
<tr>
<th>Compositions:</th>
<th>Bleaching efficiency, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basic composition containing EDTA and 10% perborate</td>
<td>29</td>
</tr>
<tr>
<td>Basic composition containing ATA, copper and 10% perborate</td>
<td>45</td>
</tr>
<tr>
<td>Basic composition containing ATA, copper and 6% perborate</td>
<td>36</td>
</tr>
</tbody>
</table>

### Example 2

To separate portions of the basic detergent formulation indicated in Example 1, there are added 0.2% by weight EDTA or 0.4% ATA and 0.02% anhydrous copper sulfate. To a similar third basic formulation but having a perborate concentration of only 6% by weight there is also added 0.4% ATA and 0.02% of copper sulfate. These formulations are then dissolved as in Example 1, to form washing solutions. The bleaching efficiency of each solution is observed and tabulated in Table II below.

### Example 3

Another detergent composition of the subject invention is made of the following formulation. It exhibits highly efficient bleaching action when used at the boil.

- Sodium tetrapropylene sulfonate... 31%
- Sodium tripolyphosphate... 35%
- Sodium silicate... 5.8%
- Sodium perborate tetrahydrate... 10%
- Copper sulfate in an amount corresponding in relation to the entire composition of 200 p.p.m. of Cu.
- ATA in an amount corresponding for each atom of Cu, of 5 molecules.
- Fluorescent dye, perfume, sodium sulfate and moisture... Balance to 100%

### Example 4

The following formulation also exhibits enhanced bleaching action at the boil.

- Condensation product of tall oil with 15 moles of ethylene oxide... 4%
- Sodium tripolyphosphate... 40%
- Sodium silicate... 7%
- Sodium perborate tetrahydrate... 10%
- Copper nitrate in an amount corresponding in relation to the entire composition of 60 p.p.m. of Cu.
- Methylaminodiacetic acid in an amount corresponding for each atom of Cu of 12 molecules.
- Fluorescent dye, perfume, sodium sulfate and moisture... Balance to 100%

### Example 5

Another detergent composition of the subject invention is made of the following formulation. It also exhibits enhanced bleaching action at the boil.
What is claimed is:
1. A stable, substantially dry, perborate-containing detergent composition effective for washing at the boil, consisting essentially of by weight from about 4 to 40% of a member selected from the group consisting of water-soluble, synthetic, non-soap anionic and nonionic organic detergents, from about 3 to about 20% water-soluble inorganic perborate, from about 40 to about 90% water-soluble inorganic alkali metal non-oxidizing builder salts, a water-soluble inorganic copper salt, and a sequestering agent selected from the group consisting of methylaminodiacetic acid, aminotriacetic acid, and hydroxyethylaminodiacetic acid, the copper salt being present in amount sufficient to produce a copper atom concentration of from about 30 to 300 parts per million parts by weight of the detergent composition, and the sequestering agent being present in amount such that 3 to 15 molecules thereof are contained in the detergent composition per atom of copper, said amounts of copper salt and sequestering agent enhancing the bleaching action of the perborate at the boil.
2. A composition according to claim 1 in which the perborate is sodium perborate tetrahydrate and the water-soluble copper salt is copper sulfate.
3. A composition according to claim 1 in which the detergent is a sodium salt of an alkyl aryl sulfonate containing from 10 to 16 carbon atoms in the alkyl group.
4. A composition according to claim 1 in which the concentration of copper is from 40 to 80 parts per million parts by weight of the detergent composition, and the sequestering agent is present in amount such that 10 to 13 molecules thereof are contained in the detergent composition per atom of copper.
5. A stable substantially dry perborate-containing detergent composition effective for washing at the boil, consisting essentially of by weight from 4 to 40% of a sodium salt of a higher alkyl benzene sulfonate containing from 10 to 16 carbon atoms in the alkyl group, from 3 to 20% sodium perborate tetrahydrate, from 40 to 90% water-soluble inorganic alkali metal non-oxidizing builder salts, copper sulfate and a sequestering agent selected from the group consisting of methylaminodiacetic acid, aminotriacetic acid, and hydroxyethylaminodiacetic acid, the copper salt being present in amount sufficient to produce a copper atom concentration of from 40 to 80 parts per million parts by weight of the detergent composition, and the sequestering agent being present in amount such that 10 to 13 molecules thereof are contained in the detergent composition per atom of copper, said amounts of copper salt and sequestering agent enhancing the bleaching action of the perborate at the boil.

References Cited by the Examiner

UNITED STATES PATENTS
2,240,957 5/41 Munz 252-99 XR
2,498,344 2/50 Rider et al. 252-99 XR
2,542,385 2/51 Ayo et al. 252-89
2,975,139 3/61 Kaufmann et al. 252-99
3,156,654 11/64 Konecny et al. 252-95

FOREIGN PATENTS
765,750 1/57 Great Britain.

OTHER REFERENCES

JULIUS GREENWALD, Primary Examiner.
ALBERT T. MEYERS, Examiner.