This invention relates to cleaning and detergent compositions which comprise anhydrous sodium carbonate in the form of porous, free flowing granules, said granules being impregnated with at least one of the classes consisting of surface-active polyoxyethylene compounds, surfactant-carboxylic acid compounds, wetting agents, and alkaline cleaners such as solutions of sodium hydroxide, the impregnation of the granules being carried out at temperatures above the liquefaction point of the material to be absorbed, and, in some cases, with the aid of a volatile solvent or other, the finished product consisting essentially of free flowing sodium carbonate granules carrying substantial amounts of the surface-active or cleaning material in the pores, fissures and other capillary recesses of the granule, all as is more fully hereinafter set forth and as claimed.

Attention is drawn to my U.S. Patent 2,992,992, Curtin, July 18, 1961, which has some points in common with the present invention.

Among the objects of the present invention are:

(1) To produce exceptionally low cost detergents of the soap type by avoiding the manufacturing expense of converting fats into soap;

(2) To produce a soap type detergent with no upper limit on the amount of unsaturated fatty acid present. This cannot be done by the process of U.S.P. 2,992,992 which can tolerate only small amounts of unsaturated fatty acids;

(3) To produce a completely dust free detergent;

(4) To make available, in free flowing, solid form, detergents and cleaners which, because of their waxy or gummy nature, are presently available only in solution form;

(5) To produce a low cost cleaning compound which will be based upon sodium carbonate but will have the higher alkalinity of the more costly sodium phosphates and silicates.

The porous granules of sodium carbonate mentioned above are of various shapes, such as, hollow spheres, biscuit-shaped granules and the like, all with fairly rough surfaces. In size, a typical batch will all pass through a 10-mesh sieve, all but 1 or 2 percent through a 20-mesh sieve and, of the material through a 20-mesh sieve, a 40-mesh sieve, 1600 openings per square inch, will pass about 45 percent and retain about 55 percent. The material through a 40-mesh sieve may be described as a powder while that retained by the same sieve may be called a coarse powder, the individual particles being somewhat smaller than gunpowder or black blasting powder.

A cubic foot of the unscreened sodium carbonate granules weighs about 32 pounds, giving a bulk specific gravity of about 0.51—0.52. The individual granules are heavier, however, as they sink when added to water. Sodium carbonate in this form is almost dust free and is now being manufactured commercially in substantial quantities. I have found that the absorption of surface active fatty and other carboxylic acids, and also other organic substances, is greatly increased by heating both the carboxylic acid and the granular sodium carbonate to a temperature in the range from slightly above the liquefaction point of the organic substance to about 150° C. The capillary openings in the granules do not tend to close upon heating but open wider, thus facilitating and increasing the absorption of the molten carboxylic acid or other substance.

Some very desirable detergent material are in waxy or gummy form at ordinary temperatures and form viscous liquids upon heating. Such materials are best dealt with by adding a small amount of a volatile solvent of which a great many are suitable. The alcohols from methanol to n-pentanol are useful, the latter boiling at about 138° C. In some cases, water may be used as the solvent. Such materials greatly reduce the viscosity of the detergent material and the absorption of the latter may be increased by 50 percent or more by this means. Usually 5 to 10 percent of the volatile solvent is sufficient, based upon the weight of the detergent. Much higher percentages, for example, 30 percent, may be used in exceptional cases.

If exceptionally high absorption of the detergent material is desired, a partial vacuum is of the greatest assistance. High vacuums are usually not necessary, a pressure of about 15 to 100 mm. of mercury being sufficient. The vacuum is applied before the start of the introduction of the detergent and is maintained until all had been added. Air is then gradually added until atmospheric pressure is reached.

In regard to the mechanism whereby the detergent-forming or cleaning material is converted into the necessary aqueous solution when added to water, in the case of a water-soluble non-ionic substance such as a polyethoxy derivative of lauric acid, this material, present in the sodium carbonate granule in very thin layers with a high ratio of surface to mass, passes at once into solution as the granule dissolves. In the case of an aqueous solution, such as, sodium hydroxide solution, held within the granule, this solution merely becomes diluted when brought into contact with water.

The various carboxylic acids of value in the present invention, are usually insoluble in water. When absorbed in liquid form by the sodium carbonate granules, such materials largely or entirely persist as free carboxylic acids since there is no water present to facilitate the usual ionic reaction. When the sodium carbonate granules containing such carboxylic acids are added to water, an immediate reaction takes place with formation of a detergent or surface-active solution. For example, in the case of palmitic acid, the reaction is as follows:

\[ C_{15}H_{31}COOH + Na_2CO_3 \rightarrow C_{15}H_{31}COONa + NaHCO_3 \]

The formation of a minor amount of sodium salt at the time of impregnation is not ruled out as it is possible in some cases, especially with unsaturated acids, there may be some sodium salt formation at this time, although there is no visual evidence of it. If so, it exists as a monomolecular layer lining the capillary openings in the granule and insulating the sodium carbonate from further contact with the carboxylic acid.

To show that a large part of the carboxylic acid absorbed by the sodium carbonate granules remains as free acid until wetted, the following qualitative experiment was performed:

To a liter beaker nearly full of water at 60° C., there was added by pouring in quickly 50 grams of the product of Example 1. The beaker and contents remained thereafter undisturbed. The granules settled to the bottom and, after a short time, a film of liquid insoluble fatty acid collected at the surface. After standing over night and cooling to 18° C., the film hardened to solid fatty acid.

As there was a considerable amount of this and more fatty acid had been converted into the sodium salt, this shows that a large part, and perhaps nearly all, of the fatty acid was in the form of free acid up to the moment
when brought into contact with water. If the addition of the granules had been accompanied by some turbulence, all of the fatty acid would have been converted to sodium salt.

To facilitate the chemical engineering equipment required for bringing about the absorption of the detergent or cleaning material by the sodium carbonate granules, this can be of the simplest and most inexpensive type. All that is required is apparatus which exposes a constantly changing surface of granules to the wetting action of a fine spray of the material to be absorbed. This material is then drawn into the interior of the granule by capillary forces.

For example, an open steel tank with a screw type elevator which will lift up quantities of granules from the bottom and spill them over the top will do. The top of the mass will be constantly wetted with a fine spray of the material to be absorbed until the desired amount of the latter has been added. The uniform distribution of the material is greatly aided by the granules since those which have too little will rob those which have too much.

Another type of apparatus is a slowly revolving steel drum, designed to provide rotation per minute, with baffles, shelves or ledges attached to the interior sides which will elevate the granules and release them in showers when a baffle reaches the horizontal position. A circulation of granules from end to end is also desirable and may be produced by setting the baffles at a suitable angle. The spray is introduced at an end, or at both ends, of the cylinder, the spray apparatus usually being unattached thereto.

When absorption is complete, the granules, usually at an elevated temperature, are discharged to a cooling apparatus. Cooling may be accomplished by causing the granules to move counter to a current of air. There is an abundance of available equipment to accomplish this purpose.

A cylinder of the type described, 12 feet in length and 8 feet in diameter, operating continuously on a 20 minute per batch cycle, with a charge of granules occupying one fourth the volume of the cylinder, can easily produce more than 300,000 pounds of impregnated granules per day.

In cases where a heavy impregnation of the granules is desired, the time per batch may be increased to 30-35 minutes.

Where a higher rate of production is sought, it is obvious that, by slight modifications, the apparatus described may be adapted to continuous operation, instead of batch.

It is often desirable to add relatively small amounts of detergent builders to the impregnated granules, such materials as the polyphosphates of soda, especially tetrasodium pyrophosphate and pentasodium tripolyphosphate, the silicates of soda, soda ash, ethylenediaminetetraacetic acid tetrasodium salt and sodium carboxymethylcellulose being particularly advantageous. These substances may be added to the batch any time after impregnation is complete to the time when the finished batch is discharged from the cooling apparatus. Such materials should be finer than 40 mesh and do not make the product dusty as the particles adhere to the surface of the granules.

The following procedure describes a specific embodiment of my invention, using the materials of Example 1:

Using the 12' by 8' cylinder above described which has been given a heat insulating covering over all practicable areas, and with the absorption to be carried out at 100–105° C., mainly, 4800 pounds of granules, one-fourth of cylinder capacity, is charged to the cylinder, the granules having been preheated to 110–115° C., 2664 pounds of the fatty acid material, also preheated to 110–115° C., is then added to the cylinder while it revolves twice per minute, addition of fatty acid being complete in 30 minutes. The cylinder is permitted to revolve for an additional 5 minutes, then the batch is discharged into the cooling cylinder. This is a revolving steel shell, 6 feet in diameter and 60 feet long, with baffles attached to the interior walls in such fashion as to lift up and cascade downward the impregnated granules while slowly moving them to the exit end. A cooling current of air passes counter to the granules. When discharged, they are free flowing and carry 55.5 pounds of fatty acid for each 100 pounds of untreated granules. This is equal to 60 pounds of sodium salt, or anhydrous soap.

In this case, the temperature in the impregnating cylinder is maintained by insulation and by charging the materials at a somewhat higher temperature. In other cases, the cylinder temperature and contents may be maintained by application of external heat.

The following examples, given for purposes of illustration, only, show various detergent, surface-active and cleaning materials which are efficiently absorbed by the sodium carbonate granules. Absorption of these materials will vary from about 2 to 70 parts by weight per 100 parts by weight of untreated granules. In no case is the maximum possible absorption given but only the actual, desired absorption as determined by small scale experiment. Unless otherwise indicated, the granules had been passed through a 40 mesh sieve. All materials are given in parts by weight. Temperature is in centigrade degrees.

**Example 1**

<table>
<thead>
<tr>
<th>Parts</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium carbonate granules</td>
<td>100</td>
</tr>
<tr>
<td>Tallow acids</td>
<td>27.75</td>
</tr>
<tr>
<td>Stripped coconut acids</td>
<td>27.75</td>
</tr>
</tbody>
</table>

The temperature of impregnation was 100–105° C. The fatty acid is equal to 60 parts of anhydrous soap.

**Example 2**

<table>
<thead>
<tr>
<th>Parts</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium carbonate granules</td>
<td>100</td>
</tr>
<tr>
<td>Stripped coconut acids</td>
<td>50</td>
</tr>
</tbody>
</table>

The temperature of impregnation was 90–95° C. The acids equal 55 parts anhydrous soap. The stripped acids have acids with less than 12 carbon atoms removed.

**Example 3**

<table>
<thead>
<tr>
<th>Parts</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium carbonate granules</td>
<td>100</td>
</tr>
<tr>
<td>Tallow acids</td>
<td>48</td>
</tr>
</tbody>
</table>

The temperature of impregnation was 95–100° C. The acids equal 52 parts of anhydrous soap.

**Example 4**

<table>
<thead>
<tr>
<th>Parts</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium carbonate granules, parts unsifted</td>
<td>100</td>
</tr>
</tbody>
</table>
| 40% caustic soda solution                  | parts...

The temperature of impregnation was 20° C. This is a cleaning material which gives aqueous solutions of pH decisively higher than possible to obtain with sodium carbonate, alone. The caustic solution may range from 5 to 50% of the wt. of the granules.

**Example 5**

This is Example 4 to which has been added the step of a second impregnation with a wetting agent, a polyoxyethylene derivative of nonylphenol carrying 10 oxyethylene groups. This provides not only higher alkalinity but also much better wetting properties. The nonylphenol derivative was in the amount of 5 parts per 100 parts of granules and was thinned with 10% of its weight of propanol-2. Impregnation also at 20° C.

In the following examples involving maleates, these compounds are formed by causing a primary alcohol to react with maleic anhydride for 5 or 10 minutes at 120–125° C., using the anhydride in one or two percent excess over the theoretical. The anhydride starts to sublime below 100° C. and loss from this source must be prevented. The reaction is quantitative with respect to the alcohol and the product, a monoster monocarboxylic
acid, may be used immediately in the molten condition for the impregnation of sodium carbonate granules.

**Example 6**

<table>
<thead>
<tr>
<th>Parts</th>
<th>100</th>
<th>38</th>
<th>3.8</th>
</tr>
</thead>
</table>
| Sodium carbonate granules | n-Dodecyl hydrogen maleate | Propanol-2 | 5 acid, may be used immediately in the molten condition for the impregnation of sodium carbonate granules. 

Impregnation was at 55 degrees, the two organic materials being dissolved together. The product was an unsurpassed detergent, usable over a wide pH range and with abundant suds.

**Example 7**

<table>
<thead>
<tr>
<th>Parts</th>
<th>100</th>
<th>35</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium carbonate granules</td>
<td>“Oxo” tridecyl hydrogen maleate</td>
<td>Propanol-2</td>
</tr>
</tbody>
</table>

Impregnation was at 50 degrees. The product was a very good detergent with slightly less suds than that of Example 7. The propanol is all lost by vaporization during the cooling.

**Example 8**

<table>
<thead>
<tr>
<th>Parts</th>
<th>100</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium carbonate granules</td>
<td>Lauramidoethylene hydrogen maleate</td>
<td>Propanol-2</td>
</tr>
</tbody>
</table>

Impregnation temperature was at 60. The amido compound is C<sub>9</sub>H<sub>19</sub>CO.NH.CH<sub>3</sub>CH<sub>2</sub>O.CO.CH.CH<sub>2</sub>OH. When converted to the sodium salt in solution, it is a powerful detergent with abundant suds, usable from pH 6 to pH 12.

**Example 9**

<table>
<thead>
<tr>
<th>Parts</th>
<th>100</th>
<th>36</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium carbonate granules</td>
<td>Nonylphenoxypolyethoxy hydrogen maleate</td>
<td>Propanol-2</td>
<td></td>
</tr>
</tbody>
</table>

There were 4 oxyethylene groups in the molecule. Impregnation temperature was 50–60. This material is a gummy mass at room temperature. The product was a fine detergent with abundant suds.

**Example 10**

<table>
<thead>
<tr>
<th>Parts</th>
<th>100</th>
<th>30</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium carbonate granules</td>
<td>“Oxo” tridecyl polyethoxymethanol</td>
<td>Propanol-2</td>
<td></td>
</tr>
</tbody>
</table>

Impregnation was at 65 degrees. The product was a light duty detergent with scanty suds. Fifteen oxyethylene groups were in the molecule. There is a great array of the polyethoxy surfactants, most of them light-duty detergents, based on alkyl phenols, fatty acids, amines, amides, and alcohols and the like. All can be processed as shown in Example 10. In most cases, carrying out the impregnation at 80–100° C. makes the use of the propyl alcohol unnecessary.

**Example 11**

<table>
<thead>
<tr>
<th>Parts</th>
<th>100</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium carbonate granules</td>
<td>2-ethylhexanol</td>
<td></td>
</tr>
</tbody>
</table>

Impregnation temperature was 30. This material is a defoamer. Other defoamers, such as tributyl phosphate and the silicone antifoamers, can be dealt with similarly.

**Example 12**

<table>
<thead>
<tr>
<th>Parts</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium carbonate granules</td>
<td></td>
</tr>
</tbody>
</table>

This impregnation was carried out at 95–100 degrees under a partial vacuum of 30–50 millimeters of mercury. After the fatty acids had been added, air was slowly admitted until the pressure was normal. These acids equal 71.7 parts of anhydrous soap. This product, like those of the other examples, was in the form of free-flowing granules.

The process described herein is, in the case of the fatty acids, the least expensive way of passing from an animal or vegetable fat to an aqueous soap solution. The difficult operations of making soap and converting it into a powder acceptable to the consumer are completely eliminated. There is substituted, instead, a relatively inexpensive passage from the fats to the fatty acids, followed by the extremely low cost absorption by sodium carbonate granules herein described.

The products of the present invention have been tested in the washing of textiles and dishes and in various cleaning operations. In all cases, the materials came up to the very best expectations.

What I claim is:

1. A free-flowing and substantially dustless cleaning composition consisting of sodium carbonate in the form of porous granules having absorbed chiefly within their capillary structures from about 5 to about 50 parts by weight of a 40% aqueous solution of sodium hydroxide per 100 parts by weight of untreated granules, said cleaning composition, when dissolved in water, having a higher alkalinity than a sodium carbonate solution and being an efficient cleaner.

2. The cleaning composition of claim 1 wherein the granules have absorbed, in addition to sodium hydroxide solution, five parts per 100 parts of said granules of a polyoxyethylene derivative of nonylphenol having 10 oxyethylene groups.

3. A process for converting sodium carbonate in the form of porous granules into a cleaning composition, which comprises agitating porous granules of sodium carbonate with about a 40% sodium hydroxide solution until the granules have absorbed about 5 to 50% by weight of the solution, and then impregnating the treated granules with a polyoxyethylene derivative of nonylphenol having 10 oxyethylene groups until the granules have absorbed about 5% by weight of the nonylphenol derivative.

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JULIUS GREENWALD, Primary Examiner.