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3,758,408
NON-YELLOWING DETERGENT FORMULATION
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### ABSTRACT OF THE DISCLOSURE

A method for substantially reducing or entirely eliminating the yellow discoloration usually associated with the repeated laundering of cotton fabrics with detergents containing a substantial amount of sodium carbonate 15 builder is disclosed. The new method includes the incorporation of titanium dioxide into the carbonate containing detergent system in an approximate weight ratio of 1:4 with the sodium carbonate builder.

## BACKGROUND OF THE INVENTION

The invention pertains to particulate heavy duty detergent formulations of the type including synthetic surface active agents and detergent builders. More specifically, 25 a primary objective of the invention is to overcome discoloration problems associated with the use of carbonate builders in synthetic detergent formulations.

Typically, most heavy duty detergents presently in use contain a substantial amount of phosphorous containing 30 material to soften the wash water and to provide detersive action in conjunction with an anionic surface active agent. The most commonly used, and most effective, of these materials are tripolyphosphates used in combination with the higher alkyl benzene sulfonates. Although the 35 foregoing detersive combination is very effective in removing soil from textile fabrics, the efficacy of discharging large amounts of phosphates into natural bodies of water is presently being examined. According to some investigators, the presence of high phosphate concentra- 40 tions in natural water bodies promotes the rapid and excessive growth of marine plant life which consumes an inordinately large amount of the oxygen present in the water, resulting in other forms of marine life being deprived of the oxygen necessary for their survival. This process, technically known as eutrophication, is currently under intensive study by private and governmental organizations. As a result of these studies it might eventually be necessary and desirable for the phosphate content of heavy duty powdered detergents to be substantially reduced or possibly eliminated entirely.

Of the substitutes for phosphate detergent builders that have been suggested in the art, sodium carbonate is appealing since it is relatively inexpensive and, in combination with nonionic surfactants, such as ethoxylated alcohols, provides effective detersive action. However, although the efficacy of sodium carbonate as a detergent builder has been known for a long time, it has seen very little use in heavy duty powdered detergents made available to the public. Apparently, a major reason for the reluctance of the industry to utilize sodium carbonate in detergent formulations on a large scale is the fact that after the repeated washing and ironing of light colored

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cotton fabrics with carbonate containing detergents, a definite yellow discoloration of the fabric appears. It is the primary objective of the present invention to solve the problem of yellowing typically associated with the use of the carbonate detergent builders in heavy duty powdered detergent formulations.

### SUMMARY OF THE INVENTION

In accordance with the invention, the yellow discolora-10 tion of cotton fabrics usually associated with carbonate containing detergents is eliminated or substantially reduced by incorporating a small amount of titanium dioxide into the detergent blend. Most advantageously, oil dispersible titanium dioxide is used in the new formulations, although a significant reduction in the discoloration of cotton fabrics has also been obtained with water dispersible titanium dioxide. Although the amount of titanium dioxide added to the carbonate containing detergent formulation can be varied within wide limits, be-20 tween about 1 part titanium dioxide to 10 parts sodium carbonate to about 1 part titanium dioxide to 2 parts sodium carbonate it has been found that a weight ratio of 1 part titanium dioxide to every 4 parts of sodium carbonate builder present in the detergent formulation is probably optimum. The presence of more than 1 part titanium dioxide per 4 parts sodium carbonate does not seem to result in any significant improvement over the preferred 1:4 ratio while a titanium dioxide to sodium carbonate, ratio of less than 1:4, although useable in accordance with the invention, does not seem to be as effective as the preferred 1:4 ratio, although improved whiteness is apparent relative to a sodium carbonate formulation without the titanium dioxide additive.

# DESCRIPTION OF PREFERRED EMBODIMENTS

In accordance with the presently preferred embodiments of the invention, about 1 gram of titanium dioxide per 4 grams of sodium carbonate is added to the powdered detergent formulation in order to eliminate the yellow discoloration of cotton fabrics that appears after repeated laundering with carbonate containing detergents.

Repeated laundering of white cotton textile fabrics with washing mediums including 1 gram of oil dispersible titanium dioxide per 4 grams of sodium carbonate have shown that the whiteness of the fabric is substantially the same after laundering as before laundering. More specifically, after ten washings in a washing medium including sodium carbonate and oil dispersible titanium dioxide in a 4:1 weight ratio, and subsequent ironing, a 50 swatch of white cotton textile fabric exhibited the same whiteness characteristics as when washed and ironed ten times in a washing medium which comprised plain tap water. It therefore appears that the presence of oil dispersible titanium dioxide in a weight ratio of 1:4 with the sodium carbonate present in the formulation completely eliminates the yellowing phenomena associated with sodium carbonate containing heavy duty detergents.

When substantially identical white cotton fabric is washed in the same manner and with the same sodium carbonate containing washing medium, except without the titanium dioxide additive, a definite and readily observable yellow discoloration of the fabric is present. Similar wash tests, using water dispersible instead of oil dispersible titanium dioxide have also been performed. Although a

marked, and usually observable reduction in the amount of fabric yellowing has been obtained with the water dispersible additive, the results have not been as favorable as with the oil dispersible titanium dioxide.

Although the cause of the yellow discoloration of cotton fabrics when repeatedly laundered in sodium carbonate containing detergents is not fully understood, it is believed to be due to the deposit of Fe ions on the cotton fibers of the fabric and the chemical linkage of these metal ions with the cellulosic structure of the fabric fibers. 10 The deposit of Fe ions on the cotton fibers when sodium carbonate is present in the washing medium, is believed to be due to the formation of insoluble carbonate compounds by the magnesium and calcium ions that are usually present in the wash water, and the carbonate. At 15 least some of these ions settle out on the fabric taking some Fe ions with them. When the Fe ions are brought into physical contact with the cellulose molecules of the cotton fibers, a chemical bond seems to be formed. The Fe ions are retained by the fabric and accumulate from wash to wash to eventually produce a visible discoloration of the fabric.

In accordance with the invention, the presence of titanium dioxide in the sodium carbonate containing washing medium effectively prevents the occurrence of this characteristic fabric discoloration after repeated launderings. Although the actual mechanism by which the titanium dioxide achieves this objective is not known, it is believed that the titanium dioxide either prevents formation of the insoluble calcium and/or magnesium carbonate compounds or renders the Fe ions unavailable for deposition on the fibers of the cotton fabric.

The solution of the yellowing problem associated with fabrics that have been repeatedly laundered with sodium 35 carbonate containing detergents permits the widespread utilization of this detergent builder in place of, either partially or completely, the currently widely used phosphates. Although the phosphate builders are very effective in combination with synthetic detergents, most advantageously anionic surfactants, their alleged contribution to water pollution might result in their eventual elimination from detergents. By utilizing the teachings of the invention sodium carbonate can be used as at least a par- 45 tial substitute for phosphate builders. Very effective nonyellowing non-phosphate containing detergent formulations in accordance with the principles of the invention have been formulated by utilizing a nonionic surfactant in combination with sodium carbonate builder in the 50following proportions:

Percent by	weight	
Sodium carboate		
Sodium sulfate	20-40	
Titanium dioxide	5-15	1
Nonionic surfactant	5-25	

A preferred formulation would have the following approximate composition:

Percent by weight		•
Sodium carbonate		
Sodium sulfate	30	
Titanium dioxide	10	
Nonionic surfactant	20	•

The nonionic surfactant is preferably an ethoxylated alcohol having an alkyl chain of from 12–18 carbon atoms and 10–19 ethylene oxide units. Suitable nonionic materials are available from the Shell Chemical Company under the trademark Neodol 45–11 (14–15 carbon atom alkyl chain, average of 11 ethylene oxide units) and from the Continental Oil Company under the trademark Alfonic 1618–78 (16–18 carbon atom alkyl chain, average of 19 ethylene oxide units). Although nonionic detergents 75

are preferred because of their effectiveness in combination with sodium carbonate builders, the commonly used synthetic anionic as well as cationic surfactants can be utilized in the new detergent formulations, either in whole or partial substitution for the preferred nonionics.

The nonionic surfactants preferred for use in combination with sodium carbonate builder and titanium dioxide to produce a non-yellowing, low phosphate containing or phosphate free heavy duty detergent powder, in accordance with the invention, are typically viscous liquids at room temperature. Consequently, they cannot be simply added to the spray dried powdered detergent. It has also been discovered that adding the liquid nonionic to the detergent mix before spray drying i.e., in the crutcher, in an amount exceeding about 5 percent by weight, results in the discharge of black smoke from the spray tower during spray drying of the mix, which, of course is undesirable. Consequently, it is preferred to combine the liquid nonionic surfactant with the sodium carbonate builder in the form of a free flowing powder that can be added to the powdered detergent mix after spray drying. In this regard, a post addable, free flowing pre-mix comprising approximately 33 percent by weight Neodol 45-11 and approximately 66 percent by weight anhydrous sodium carbonate powder was prepared by spraying the liquid nonionic material onto a laboratory dish containing the sodium carbonate powder and then mixing with a spatula to produce a free flowing powder. If desired, the titanium dioxide component of the final detergent formulation can be mixed with the sodium carbonate powder before it is combined with the liquid nonionic component, to form part of the post addable pre-mix. Additionally, the weight percent of nonionic surfactant in the free flowing premix can be increased to about 50 percent by including a small amount, typically less than about 10 percent by weight, and preferably about 5 percent by weight, of microsized silica particles, such as pyrogenic silicon dioxide as made available by the Cabot Corporation, under the trademark Cab-O-Sil grade EH-5, in the sodium carbonate powder prior to its combination with the liquid nonionic surfactant. A representative pre-mix formulation in accordance with the specific aspect of the invention would be as follows:

Percent by w	
Neodol 45–11	45.0
Sodium carbonate	40.0
Pyrogenic silicon dioxide	
Oil dispersible titanium dioxide	

The foregoing pre-mix is in the form of a free flowing powder that is very suitable for post addition to spray detergent powders.

The foregoing specific examples are intended to be representative only and not limiting of the invention. For example anionic water soluble synthetic detergents, such as the higher alkyl benzene sulfonates can be utilized in place of, and in the same amount by weight as the preferred nonionic surfactant in the foregoing examples. Similarly, water soluble cationic surfactants, such as the quaternary ammonium salts can be substituted for the preferred nonionic surfactants. Accordingly, reference should be made to the following claims in determining the full scope of the invention.

We claim:

- 1. A detergent formulation suitable for cleaning cotton textile fabrics consisting essentially of,
  - (a) from about 5 to 25 percent by weight of a nonionic synthetic surface active agent,
  - (b) from about 10 to about 50 percent by weight of sodium carbonate builder, and
  - (c) from about 5 to about 15 percent by weight of tianium dioxide

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- (d) the weight ratio of sodium carbonate to titanium dioxide being from about 2:1 to about 10:1.
- 2. The detergent formulation of claim 1 wherein, (a) said titanium dioxide is oil dispersible.
- 3. The detergent formulation of claim 1 wherein said 5 synthetic detergent is a nonionic surfactant chosen from the group consisting of ethoxylated alcohols having an alkyl chain of from about 12 to 18 carbon atoms and an average of from about 11 to 19 ethylene oxide units.

4. The detergent formulation of claim 1 wherein the weight ratio of sodium carbonate to titanium dioxide is about 4:1.

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