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Patents Act 1990
PATENT REQUEST : STANDARD PATENT

We, being the person(s) identified below as the Applicant, request the grant of a patent to the person identified below as the Nominated Person, for an invention described in the accompanying standard complete specification.

Applicant: PROTEIN TECHNOLOGIES INTERNATIONAL, INC.
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Nominated Person: As above
Address: As above

Invention Title: METHOD OF IMPROVING THE SOIL ANTI-REDEPOSITION PROPERTIES OF WASHING DETERGENTS AND PRODUCTS

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BASIC CONVENTION APPLICATION DETAILS
Applicants' Name: to be advised
Application Number: 749,746
Country: United States of America
Code: US
Date of Application: 26th August, 1991

Dated this 28th day of October, 1991.

CARTER SMITH & BEADLE
Patent Attorneys for the Applicant

Our Ref: #9298 DCC:WB 10–12pro
NOTICE OF ENTITLEMENT

I/We, PROTEIN TECHNOLOGIES INTERNATIONAL, INC., of Checkerboard Square, St. Louis, Missouri 63164, United States of America, being the applicant in respect of Application No. 86794/91, state the following:–

The person(s) nominated for the grant of the patent:

has, for the following reasons, gained entitlement from the actual inventor(s):
Thomas L. Krinski, 3309 Franklin, Granite City, IL 62040, U.S.A.; and
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by assignment etc.

The person(s) nominated for the grant of the patent:

or

has entitlement from the applicant(s) of the basic application(s) listed on the patent request form

by assignment

The basic application(s) listed on the request form:

is/are the first application(s) made in a Convention country in respect of the invention

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Dated November 2, 1991

PROTEIN TECHNOLOGIES INTERNATIONAL, INC.
Please type name and position of signatory
Larry J. Hurst, Vice President
A detergent composition and method may have the soil anti-redeposition properties significantly and unexpectedly improved by incorporating into the detergent composition an effective amount of an anti-redeposition agent. The anti-redeposition agent is a casein material which has been modified with an ionic monomer. Ionic monomers which have been found to be especially effective at improving the anti-redeposition properties of washing detergent compositions are cationic epoxide monomers, cationic acrylate monomers and cationic chlorohydrin monomers. Anionic or carboxylated casein derivatives have also been shown to be effective anti-redeposition agents.
Invention Title: METHOD OF IMPROVING THE SOIL ANTI-REDEPOSITION PROPERTIES OF WASHING DETERGENTS AND PRODUCTS

The following statement is a full description of this invention, including the best method of performing it known to us:

Our Ref: #9298 DCC:WB 10-12pro
BACKGROUND OF THE INVENTION

This application is a continuation in part application of pending application U.S. Serial No. 07/516,178 filed April 30, 1990.

This invention relates to detergent compositions and methods of forming detergent compositions. The detergent compositions formed have greatly improved soil removal and/or anti-redeposition properties. These properties have been found to be unexpectedly improved by the addition of a modified casein material which provides greatly improved and unexpected anti-redeposition properties. Further, the modified casein material is rapidly biodegradable, thus significantly improving the environmental properties of the detergent as a whole.

Applicants are aware of the following U.S. Patents, the disclosures of which are incorporated by reference herein.

U.S. Patent 3,000,830
U.S. Patent 3,594,324
U.S. Patent 4,352,692
U.S. Patent 4,474,694
U.S. Patent 4,689,381

Synthetic detergent compositions have been used commercially for many years for the removal of soil from fabric. These materials generally are combinations of a number of different compounds or
additives. These compositions may include, although they are not necessarily limited to, an organic detergent compound such as a surfactant or surface active agent, builder components such as a phosphate salt which enhances the cleaning effectiveness of the surfactant by sequestering various metal ions found in hard water and also a soil suspending or anti-redeposition agent to help the surfactant hold the soil particles in suspension and prevent them from being redeposited onto the fabric during washing.

The use of a soil anti-redeposition agent generally improves the whiteness of fabrics washed with the detergent or the brightness of the color, since the anti-redeposition agent suspends the soil in the solution once it has been removed from the fabric and prevents its redeposition onto the washed fabric. If the detergent composition has poor soil suspension properties during washing and the soil is allowed to be redeposited or to settle from the wash water onto the washed fabric, the fabric will eventually acquire a gray or dull appearance, which is extremely undesirable aesthetically.

A number of materials have been used as soil anti-redeposition agents. Once of the most widely used material is carboxymethylcellulose. Carboxymethylcellulose has been added for a number of years to different types of detergent compositions used for washing fabrics to prevent redeposition of soil from solution once the soil has been removed from the fabric by washing. Other materials which
have been proposed or used as soil anti-redeposition agents include sodium polyacrylate, polyvinyl acetate, ethylcelluloses, polyvinyl alcohols, sodium alginate and various modified starches. All of the above are generally regarded as being less effective than carboxymethylcellulose. Other types of soil anti-redeposition agents which have been described as having improved soil anti-redeposition properties over carboxymethylcellulose include polyvinylpyrrolidone, as described in U.S. Patent 3,000,830, and a combination of carboxymethylcellulose and a gelatin protein as described in U.S. Patent 3,594,324. While use of these materials as soil anti-redeposition agents in detergents has been somewhat successful, nonetheless, a need still exists for an improved material having better soil anti-redeposition properties and one which is readily adaptable and useful in a wide variety of detergent composition. It is particularly desirable to develop a soil anti-redeposition agent which is more effective in liquid detergent compositions. Carboxymethylcellulose and ethylcelluloses, for example, and other state of the art redeposition agents, typically have very poor solubility in the solutions which make up liquid detergent compositions. As a result, these materials have very low effectiveness as soil anti-redeposition agents in liquid detergent compositions.

Applicants have found that a modified casein material, particularly a modified casein material which incorporates a cationic monomer, and in particular a cationic chlorohydrin, epoxy and/or
acrylate monomers, have unexpected soil anti-redeposition properties. These soil anti-redeposition properties are observable when the material is used in liquid detergent compositions or in dry powdered detergent compositions. Moreover, these modified casein materials exhibit an unexpected improvement in soil anti-redeposition properties in many detergent systems. Applicants' anti-redeposition materials are effective in liquid and powered detergents even if used in cool or hot water. Applicants' anti-redeposition materials are effective when used with a variety of conventional washing detergent materials, including surfactants, builders and additives. Applicants' anti-redeposition materials are effective on a wide variety of soils and for a wide variety of fabrics.

It is therefore an object of the present invention to provide a method of improving the soil anti-redeposition properties of detergent compositions.

It is a further object of the present invention to provide a detergent composition which has greatly improved soil anti-redeposition properties.

It is also an object of the present invention to provide a method of improving the soil anti-redeposition properties of detergent materials by incorporating a modified casein compound in the detergent composition.
It is an object of this invention to improve the biodegradable properties of washing detergents.

It is an object of this invention to provide a modified casein soil anti-redeposition agent for washing detergents.

It is an object of this invention to provide an ionically modified soil anti-redeposition agent for washing detergents.

It is an object of this invention to provide cationically and anionically modified casein soil anti-redeposition agents for washing detergents and to provide a method using such soil anti-redeposition agents.

These and other objects will be apparent from the following Description of the Preferred Embodiments.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The unique material which is employed in the production of a detergent containing a soil anti-deposition agent is a modified casein material. These materials are obtained by modifying a casein with a cationic monomer. Epoxide, chlorohydrin and acrylate cationic monomers have been found to be particularly suitable for use in this invention.
Anionic phthalate monomers have also been found suitable for modifying the casein material in the manner generally described in U.S. 4,474,674, which describes such a reaction for vegetable protein.

The casein material which is modified pursuant to the present invention is not critical and can be selected from any type of casein including acid precipitated casein, lactic acid casein, as well as various caseinate salts such as sodium caseinate.

A fairly conventional detergent composition may be used with applicants' anti-redeposition agents to prepare either a dry powdered detergent or a liquid detergent which exhibits unexpected soil anti-redeposition properties. Such a detergent composition may be formulated by employing an organic detergent substance or surfactant. The surfactant may be chosen from any of the conventional anionic, nonionic, amphoteric or zwitterionic surfactants, which can be used alone or in combination to produce a detergent composition containing applicants' anti-redeposition agent. The following description of materials represents only illustrations of the numerous detergents which can find use with applicants' anti-redeposition agent.

The anionic organic detergent compounds or anionic surface active agents may include detergent compounds which contain an organic hydrophobic group and an ionic solubilizing group. Typical examples of ionic solubilizing groups are sulphonate, sulphate, carboxylate and
phosphate. Examples of suitable anionic detergents which would fall within the scope of the invention include the water soluble salts of higher fatty acids or resin acids such as may be derived from fats, oils and waxes of animal or vegetable origin and the sulphated and sulphonated synthetic detergents. Also included in the class of suitable detergent compounds include suitable anionic detergents such as the higher alkyl aryl sulfonates such as the alkyl benzene sulphonates as well as the sulphates of higher alcohols such as sodium lauryl sulfate and similar materials.

Nonionic synthetic detergent compounds do not ionize in solution and the whole molecule acts as a cleaning agent. Those compounds which can be generally or broadly used in the present invention can be broadly defined as compounds produced by the condensation of alkyloxide groups which are hydrophilic in nature with an organic hydrophobic compound which may be aliphatic or aromatic in nature. The most widely used class of noionic synthetic detergents include those which are formed by condensing ethylene oxide or propylene oxide with a hydrophobic base. However, other suitable nonionic organic synthetic detergent compounds including the polyethylene oxide condensates of alkyl phenols, as well as condensation products of materials such as ethylene oxide and the product resulting from the reaction of propylene oxide with ethylene oxide, the long chain tertiary amine oxides and the long chain alkyl phosphates may all be used with applicants' invention.
Amphoteric synthetic detergent compounds can be described as derivatives of aliphatic secondary and tertiary amines. Examples of specific compounds within this general grouping are materials such as sodium-3-dodecylaminoproprionate. Amphoteric surfactants have both positive and negative centers and assume either a positive (cationic) or negative (anionic) charge depending on the pH of the solution.

Zwitterionic synthetic detergent compounds behave similarly to nonionic surfactants and can be described as derivatives of aliphatic quarternary ammonium phosphonium, halide and sulfonium compounds. Examples of specific compounds falling within this definition are materials such as N, N-dimethyl-N-hexadecyl amino propane-1-sulfonate. These latter compounds are especially preferred for detergent characteristics in relatively cool water.

The detergent composition of the present invention can further include typical but non-limiting ingredients to improve other properties of the detergent composition. Included within this grouping of materials include compounds such that are described typically as water soluble builder salts such as phosphates which are added for purposes of enhancing the cleaning power of the detergent composition. Furthermore, various other materials may also be present such as materials to improve detergency of the composition and modify the foaming properties in whatever manner desired as well as various optical brightening agents,
fluorescent whitening agents and the like. Germicidal ingredients may also be added to improve the overall cleaning or disinfecting properties of the detergent composition of the present invention. The present invention is not intended to be limited by the exact contents of the detergent composition of the present invention since numerous materials are well known and well within the knowledge of those skilled in the art in the production of detergents.

The above general groupings of organic detergent compounds may be used singly or in combination in the practice of this invention with applicants' modified protein material. These materials represent specific illustrations of many of the numerous conventional organic detergent compounds or surfactants which can find application within the scope of the invention. These materials may be used in dry powdered washing materials or as liquid detergent washing materials, as known in the art, with the novel addition of the modified casein material to produce washing compounds having unexpectedly improved anti-redeposition properties, and in particular to produce liquid detergent compounds having greatly improved soil anti-redeposition properties.

Moreover, applicants' modified casein material permits replacement of a substantial portion of the compounds making up washing detergents with a readily biodegradable material. This significantly reduces the period that effluent detergent washing material remain the environment, since the conventional anti-redeposition materials which are replaced
break down very slowly in the environment. Applicants' anti-redeposition agents may be used at levels of from about 0.2 to 5% by weight of the detergent composition, and typically would be used at a level of from about 0.5 to 2% by weight of the total formulation, though the amount is not critical. Since applicants' product will break down in the environment in a matter of days, rather than years for some petroleum base materials, a very significant and unexpected improvement in the environmental performance of the washing compound can be achieved.

The following example is given to further illustrate the specific embodiments of the present invention and the improvements achieved thereby.

**Example 1**

A liquid detergent material was formulated as follows:

- 8.3 parts Neodol 25-9 (TM, Shell Chemical)
- 16.7 parts sodium alkyl benzene sulfonate
- 73.0 parts water
- 2.0 parts anti-redeposition agent (The control did not contain an anti-redeposition agent.)
The anti-redeposition agent used was a cationic modified casein material produced as described below.

Acid precipitated casein is suspended in water to a solids level of about 3-5% by weight. The pH of the suspension is adjusted to about 9 to 10 by the addition of sodium hydroxide. To the suspension is added 3-chloro 2-hydroxypropyl trimethyl ammonium chloride in an amount of 10% by weight of the solids. The casein is reacted at a pH of 9-10 at 60°C for one hour. Following reaction the modified casein is precipitated at a pH of about 4.5 and separated.

The control detergent and the detergent composition containing the modified casein were evaluated for effectiveness in preventing the redeposition of soil on fabric during washing. Five replications of 3x3 inch white swatches of 50/50 polyester/cotton were impregnated with .01% carbon black. The swatches were then washed five cycles in a conventional test washing machine. Wash temperature was 25°C. Wash time was 10 minutes. The detergent concentration was 0.15% by weight of the wash water. The fabric was rinsed once per cycle with 10% of the wash liquor left in the swatches of fabric. The comparative results from Example 1 are set forth in Table 1.

Total redeposition measured by the reflectance of the fabric is reported. Higher numbers indicate less soil redeposited. Reflectance was measured by a Hunter Colorimeter Model #PC2A, using the Y index.
It may be seen that the modified casein of the present invention had improved redeposition properties over the control sample.

Although the present invention has been described relative to the specific embodiments set forth herein, it is intended to include within the scope of the present invention all reasonable equivalents, substitutions and modifications thereof as will be appreciated by one skilled in the art. Applicant is not to be limited by the embodiments given herein for purposes of illustration but only by the claims appended hereto and their equivalents.

The claims form part of the disclosure of this specification.
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A laundry detergent having one or more surfactants and additive materials and a soil anti-redeposition agent, which is a casein material modified by reaction with an anionic and cationic monomer, in an amount of at least about 0.2% by weight to substantially reduce the amount of suspended soil which is redeposited on washed fabric during a wash cycle.

2. The laundry detergent of claim 1 wherein the casein material is modified by a cationic monomer.

3. A laundry detergent having a surfactant and additive materials and a soil anti-redeposition agent, which is an epoxy modified casein material, in an amount effective to substantially reduce the amount of suspended soil which is redeposited on washed fabric during a wash cycle.

4. A laundry detergent having a surfactant and additive materials and a soil anti-redeposition agent, which is an acrylic modified casein material in an amount effective to substantially reduce the amount of suspended soil which is redeposited on washed fabric during a wash cycle.

5. The laundry detergent of any one of claims 1 to 4
wherein the laundry detergent is a liquid detergent.

6. The laundry detergent of any one of claims 1 to 4 wherein the laundry detergent is a powdered detergent.

7. A laundry detergent having a surfactant and additive materials and a soil anti-redeposition agent which is a casein material modified by reaction with a cationic monomer selected from the group consisting of 3-chloro 2-hydroxypropyltrimethyl ammonium chloride, 4-chlorobutene trimethyl ammonium chloride and 2,3 epoxypropyltrimethyl ammonium chloride in an amount effective to substantially reduce the amount of suspended soil which is redeposited on washed fabric during a wash cycle.

8. The laundry detergent of claim 1 wherein the casein material is modified by an anionic monomer.

9. The laundry detergent of any one of claims 1 to 8 wherein the soil anti-redeposition agent is biodegradable.

10. The washing laundry detergent substantially as hereinbefore described or having any of the features hereinbefore described.
11. A method of improving the soil anti-redeposition properties of a laundry detergent comprising one or more surfactants, comprising adding to the laundry detergent an anionic or cationic modified casein material in an amount at least about 0.2% by weight to substantially reduce the amount of suspended soil which is redeposited on washed fabric during a wash cycle.

12. An improved laundry detergent in the form of a surfactant, and any additive materials, containing, as the improvement, a casein material modified by reaction with an anionic or cationic monomer in an amount in the range of 0.2 to 5 percent by weight of the detergent effective to reduce substantially the amount of suspended soil which is redeposited on washed fabric during a wash cycle.

13. The laundry detergent of claim 12 wherein the cationic monomer is a cationic monomer selected from the group consisting of 3-chloro 2-hydroxypropyl trimethyl ammonium chloride, 4-chlorobutene trimethyl ammonium chloride and 2, 3 epoxypropyltrimethyl ammonium chloride.

14. The laundry detergent of claim 12 wherein the casein material is modified by an anionic phthlate monomer.

15. A method of improving soil anti-redeposition substantially as nereinbefore described or properties having any of the steps hereinbefore described.

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