(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 530 418 A1**

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: **91310071.5**

(51) Int. Cl.[5]: **C11D 3/384**

(22) Date of filing: **31.10.91**

(30) Priority: **26.08.91 US 749746**

(43) Date of publication of application:
10.03.93 Bulletin 93/10

(84) Designated Contracting States:
BE DE ES FR GB IT

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(54) **Method of improving the soil anti-redeposition properties of washing detergents and products.**

(57) A detergent composition may have its soil anti-redeposition properties significantly and unexpectedly improved by incorporating into it an effective amount of an anti-redeposition agent which 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.

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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. In accordance with the invention, these properties have been found to be unexpectedly improved by the addition to the detergent compositions of a modified casein material which provides greatly improved and unexpected anti-redeposition properties. Further, the modified casein material added in accordance with the invention is rapidly biodegradable, thus significantly improving the environmental properties of the detergent as a whole.

The following U.S. Patents are believed to be relevant prior art:

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 compositions are generally combinations of a number of different compounds or additives. They 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 colour, 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, and the detergent will be perceived by the consumer as ineffective.

A number of materials have been used as soil anti-redeposition agents. One of the most widely used materials 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. Although the 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. Moreover, in view of the increased public concern in recent years for the environment, it is highly desirable that any such agent should be biodegradable, obtainable from "renewable" resources, and, in general, be environmentally friendly.

We have found that a modified casein material, particularly a modified casein material which incorporates a cationic monomer, and in particular cationic chlorohydrin, epoxy and/or acrylate monomers, has unexpected soil anti-redeposition properties. These soil anti-redeposition properties are observable when the material is used in all forms of detergent compositions, notably 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. The anti-redeposition materials of the present invention are effective in liquid and powered detergents even if used in cool or hot water. The anti-redeposition materials are effective when used with a variety of conventional washing detergent materials, including surfactants, builders and additives; they are also effective on a wide variety of soils and for a wide variety of fabrics.

Accordingly, the present invention provides a laundry detergent comprising one or more surfactants and optionally additive materials and including a soil anti-redeposition agent, characterised in that the soil anti-redeposition agent is a casein material modified by reaction with an anionic or cationic monomer, preferably in an amount of at least 0.2% by weight to substantially reduce the amount of suspended soil which is redeposited on washed fabric during a wash cycle.

The unique material which is employed in the production of a detergent containing a soil anti-deposition agent in accordance with the present invention is a modified casein material. These materials may be 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 nature of the original casein material which is modified to prepare the additive used in 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 the anti-redeposition agents of the present invention 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 the anti-redeposition agent. The following description of materials represents only illustrations of the numerous detergents which can find use with the 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 could be used in the detergent composition 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 are suitable anionic detergents such as the higher alkyl aryl sulphonates (e.g. the alkyl benzene sulphonates) as well as the sulphates of higher alcohols such as sodium lauryl sulphate 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 generally be used in the present invention can be broadly defined as compounds produced by the condensation of alkyl oxide 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 nonionic 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 the 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-dodecylaminopropionate. Amphoteric surfactants have both positive and negative centres 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 sulphonium compounds. Examples of specific compounds falling within this definition are materials such as N,N-dimethyl-N-hexadecylaminopropane 1-sulphonate. These latter compounds are especially preferred for detergent characteristics in relatively cool water.

The detergent compositions 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 are compounds which are typically described 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 the 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 the 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, the modified casein material used in the detergent composition of the present invention 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 in the environment, since the conventional anti-redeposition materials which are replaced by the present invention break down very slowly in the environment. The anti-redeposition agents of the present invention are preferably used a levels of from 0.2 to 5% by weight of the detergent composition, and typically would be used at a level of from 0.5 to 2% by weight of the total formulation, though the amount is not critical. Since the product will break down in the environment in a matter of days, rather than the period of years required for some petroleum-based materials, a very significant and unexpected improvement in the environmental impact of the washing compound can be achieved.

The following non-limiting Example is given to further illustrate the specific embodiments of the present invention and the improvements achieved thereby.

Example

A liquid detergent material was formulated as follows:

8.3 parts Neodol 25-9 (TM, Shell Chemical)

16.7 parts sodium alkyl benzene sulphonate

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 was suspended in water to a solids level of about 3 - 5% by weight. The pH of the suspension was adjusted to about 9 to 10 by the addition of sodium hydroxide. To the suspension was added 3-chloro-2-hydroxypropyl trimethyl ammonium chloride in an amount of 10% by weight of the solids. The casein was reacted at a pH of 9 - 10 at 60 ° C for one hour. Following the reaction, the modified casein was 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 3 x 3 inch (7.6 x 7.6 cm) white swatches of 50/50 polyester/cotton were impregnated with 0.01% carbon black. The swatches were then washed for five cycles in a conventional test washing machine. The wash temperature was 25 ° C, and the 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 this Example 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 #PC2Δ, using the Y index.

TABLE 1

Polymer	Wash T. ° C	Reflectance (Total R)
Modified Casein	25	66.0
Control	25	57.1

It may be seen that the modified casein of the present invention had improved redeposition properties over the control sample.

Claims

1. A laundry detergent comprising one or more surfactants and optionally additive materials and including a soil anti-redeposition agent, characterised in that the soil anti-redeposition agent is a casein material modified by reaction with an anionic or cationic monomer.

2. A detergent according to Claim 1, in which the soil anti-redeposition agent is present in an amount of at least 0.2% by weight of the detergent composition.

3. A detergent according to Claim 1 or Claim 2, in which the casein material is modified by a cationic monomer.

4. A detergent according to Claim 3, in which the cationic monomer is 3-chloro-2-hydroxypropyl trimethyl ammonium chloride, 4-chlorobutene trimethyl ammonium chloride or 2,3-epoxypropyltrimethyl ammonium chloride.

5. A detergent according to Claim 1 or Claim 2, in which the casein material is an epoxy-modified casein material.

6. A detergent according to Claim 1 or Claim 2, in which the casein material is an acrylic-modified casein material.

7. A detergent according to Claim 1 or Claim 2, in which the casein material is modified by an anionic monomer.

8. A detergent according to Claim 7, in which the casein material is modified by an anionic phthlate monomer.

9. A detergent according to any one of the preceding Claims, which is a liquid detergent.

10. A detergent according to any one of Claims 1 to 8, which is a powdered detergent.

11. A detergent according to any one of the preceding Claims, in which the soil anti-redeposition agent is biodegradable.

12. A detergent according to any one of the preceding Claims, in which the soil anti-redeposition agent is present in an amount of from 0.2 to 5 percent by weight of the detergent composition.

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EUROPEAN SEARCH REPORT

Application Number EP 91310071.5

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	DERWENT ACCESSION NO. 78-14 873A, Questel Telesystems (WPI), DERWENT PUBLICATIONS LTD., London * Abstract * & JP-A-53-002 506 (IDEMITSU INDUSTRIES KK et al.) --	1,2,7, 9,12	C 11 D 3/384
Y		3-6,8, 10,11	
X	DERWENT ACCESSION NO: 79-45 046B, Questel Telesystems (WPI), DERWENT PUBLICATIONS LTD., London * Abstract * & JP-A-54-056 612 (LION FAT & OIL KK) --	1-4,12	
Y		5-11	
D,Y	US - A - 4 689 381 (T.L. KRINSKI et al.) * Claims 1,11,12 * --	3-6	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
D,Y	US - A - 4 474 694 (C.E. COCO et al.) * Claims 1,11 * --	7,8	C 11 D
Y	EP - A - 0 110 007 (D. PÖTSCHKE) * Claim 1; page 2, lines 7-12; page 4, lines 9-21; page 5, line 11 - page 6, line 4 * --	9-11	
Y	DE - A - 2 937 012 (HENKEL KGaA) * Claims 1,2,7,8; page 5, lines 13-25; page 21; table 5 * --	3,5	
E	EP - A - 0 457 205	1,2,6,	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	22-09-1992	REISER

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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EUROPEAN SEARCH REPORT

Application Number

EP 91310071.5

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
	(BASF AG) * Claims 1-3; page 2, lines 46-48; examples 1-6,10; page 10, lines 24-40 * ----	7,9-12	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)

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VIENNA	22-09-1992	REISER

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