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(54) Antiredeposition agents.

(57) The disclosure relates to an antiredeposition agent to be used in detergents. The antiredeposition agent consists of a low-molecular, multi-functional ester having from 1 to 6, preferably from 1 to 3 acid units which are esterified with alcohol units. The ratio of the ester between free hydroxyl and carboxyl groups is 2—30, preferably 5—15. This is attained in that the ester contains 1—3, preferably 2—3 free hydroxyl groups/mol and 0.1—0.5, preferably 0.2—0.4 free carboxyl groups/mol. The acid units of the ester are preferably formed from phthalic acid anhydride, isophthalic acid, adipic acid, maleic acid and trimellitic acid, or mixtures thereof. The alcohol units of the ester are preferably formed from ethylene glycol, 1,2-propanediol and diethylene glycol, or mixtures thereof.

ANTIREDEPOSITION AGENTS

The present invention relates to antiredeposition agents (antigreying agents) consisting of relatively low-molecular, multifunctional esters, as well as to detergents containing such esters.

In the washing of a wash such as articles of clothing and other textiles, the dirt is removed from the wash during the washing process by chemical and physical action. The dirt is then held suspended and emulsified in the washing water in the form of small particles. In the ideal situation, the dirt is removed completely along with the washing water during the emptying operation, but since the size of the wash is often large in relation to the volume of water involved, a certain redeposition of dirt takes place onto the fibres of the wash. The redeposited dirt is normally finely-divided and manifests itself as a general greying of the textiles rather than in the form of spots or blotches. Naturally, this greying is particularly troublesome when white textiles are involved, but is also noticeable on a coloured wash, and in particular black textiles to which a grey hue is imparted.

It has been found that the redeposition of dirt is dependent upon several factors. The physical properties and chemical structure of the dirt play an important rôle, as well as the selection of surfactant and "builder" in the detergent. The perhaps most important single factor is, however, the type of fibre in the wash. Different fibres are hydrophilic to different degrees, have different Z-potential and different capacities to form hydrogen bondings, properties which are decisive for the degree of greying.

Already in the 1930ies, it was discovered that carboxy methyl cellulose (CMC) had a marked antiredeposition effect on cotton textiles. CMC is a high-polymer anionic cellulose ether which has a good antiredeposition effect in concentrations of as low as 0.5-1.0 % of the detergent composition. It is assumed that this antiredeposition effect depends upon a selective adsorption to the cotton fibres by hydrogen bonding, whereafter the negatively charged dirt particles are repelled by the carboxylate groups in the CMC. By the introduction of CMC into detergent compositions, it can be said that the problems inherent in antiredeposition have been solved as far as cotton textiles are concerned. On the other hand, CMC is practically inactive on synthetic textiles for the prevention of greying or redeposition. CMC normally displays no antiredeposition effect whatever on the most widespread synthetic fibre, polyester; and with the popular mixed textiles of the type polyester/cotton, this antiredeposition effect is slight, unless the proportion of cotton is very high in the textile.

Concurrently with the increasing use of synthetic fibres, greying has become a steadily more serious problem in the washing process. Much effort has been devoted to attempting to find antiredeposition agents which are effective on synthetic textiles, primarily of polyester fibres. A great number of different types of polymers has been tested as antiredeposition agent and, in some cases, this has led to the development of commercially viable products. Thus, for example, polyvinylpyrrolidone (PVP) polyvinyl alcohol (PVA), as well as non-ionic polyesters and cellulose ethers have been used to a certain extent. In all cases, this is a matter of high-molecular chain molecules, along the lines of CMC. However, none of the hitherto produced polymers has displayed the desired antiredeposition effect, and their use is very restricted in domestic detergents in Europe.

As an example of the prior art technology, reference might be made to Norwegian Patent Specification No. 122,199 which relates to a washing and cleaning agent which contains, as antiredeposition agent, from 0.1-20 % by weight, calculated on the total weight of the cleaning agent, of water-soluble salts of carboxyl group-containing polyesters.The ratio of carboxyl groups to hydroxyl groups is, there, greater than 1, and the polyester has a high degree of polymerisation.

In the present invention, it has now surprisingly proved that certain low-molecular (molecular weight < 1000),multi-functional esters have an antiredeposition effect on polyester fibre which is fully on a par with the effect obtained by CMC on cotton. The esters are prepared from multi-functional acids and bases, and the condensation is arrested at an early stage in order to keep the molecular weight down. A typical ester compound according to the invention contains from 1 to 6 acid units bonded with alcohol units, and a preferred compound contains from 1 to 3 acid units. The compounds according to the invention are further characterized in that the number of free hydroxyl groups/mol is from 1 to 3, preferably from 2 to 3, and in that the number of free carboxyl groups/mol is from 0.1 to 0.5, preferably from 0.2 to 0.4. Thus the ratio of free hydroxyl groups/free carboxyl groups in the finished compound is from 2 to 30, preferably from 5 to 15. The concentration of free hydroxyl and carboxyl groups in the compounds according to the invention controls, int. al., the hydrophility and the hydrogen bonding capacity of the compound and would seem to have a decisive effect on its antiredeposition properties. If the above-disclosed range limits are exceeded in one direction or the other, the effect would be drastically impaired. The physical explanation for this phenomenon is not yet known.

Further characteristic features of the present invention are apparent from the appended claims. The multi-functional esters according to the invention are manufactured in accordance with prior-art technology (please see, for example, D.H. Solomon, <u>The Chemistry of Organic Film Formers</u>, Krieger Publ., New York 1977). The starting materials comprise aliphatic, cycloaliphatic and aromatic divalent, trivalent and tetravalent carboxylic acids, as well as aliphatic and cycloaliphatic divalent, trivalent and tetravalent alcohols.

Examples of applicable acids are ortho, iso and terephthalic acid, tri and pyromellitic acid, malonic acid, succinic acid, glutaric acid, adipic acid, sebacic acid, maleic acid, fumaric acid, citric acid, nitrilotriacetic acid, cyclohexane tricarboxylic acid and ethylenediaminetetraacetic acid. Naturally, reactive derivates of these acids may also be used, such as anhydrides, esters and acid chlorides.

Preferred acids and acid derivates are phthalic acid anhydride, isophthalic acid, adipic acid, maleic acid and trimellitic acid.

Examples of applicable alcohols are ethylene glycol, 1,2-propanediol, diethylene glycol, neopentyl glycol, 1,6-hexanediol, neopentyl glycol pivallic acid ester, timethylol propane, glycerol and pentaerythritol.

Preferred alcohols are ethylene glycol, 1,2-propanediol and diethylene glycol.

The multi-functional ester according to the invention is used in combination with normal detergent raw materials such as phosphate, zeolite, silicate, surfactant, perborate, percarbonate, soda and sulphate. It can be used as sole antiredeposition agent or in combination with other such agents, for example CMC. Normally, the ester constitutes 0.1-2 % of the detergent composition.

In the manufacture of detergent, the ester according to the invention may be introduced in a variety of manners, among which mention might be made of:

a) direct admixture to the detergent slurry before spray drying of the slurry in the preparation of the detergent;

b) spraying in the warm state onto dry detergent;

c) dissolution or emulsification in water or organic solvent, whereafter the solution or emulsion is added to the above-mentioned slurry or the spray-dried detergent;

d) absorption on an inorganic carrier, for example phosphate, zeolite, silicate, soda, bicarbonate, sulphate,which is then added to the abovementioned slurry or the finished detergent;

e) admixture in organic compounds, for example polyethylene glycol and stearic acid, whereafter the mixture is added to the finished detergent;

f) admixture in a fluid detergent composition, possibly after dissolution in organic solvent or emulsification in water.

The examples below are intended to illustrate the present invention without restriction thereof.

EXAMPLE 1

Preparation of compound 1.

A mixture of isophthalic acid (120 g), trimellitic acid anhydride (140 g), ethylene glycol (70 g) and diethylene glycol (280 g) was heated at 210-220°C under nitrogen gas. The reaction was followed by means of acid number determination. When the acid number had reached the value which approximately corresponded to the formation of diethers of the included acids, the reaction mixture was cooled. Analysis of the thus obtained compound showed that the number of free hydroxyl groups/mol was 2.0 and the number of free carboxyl groups/mol was 0.27.

EXAMPLE 2

Preparation of compound 2.

A mixture of phthalic acid anhydride (269 g) and propylene glycol (380 g) was heated at 180-190°C for 5 h under nitrogen gas. The reaction mixture was cooled to 150°C, whereafter trimellitic acid anhydride (120 g) was added. The reaction was allowed to continue first at 150°C, thereafter at a higher temperature (180-200°C), until the acid number 50 had been reached. An analysis showed that the number of free hydroxyl groups/mol was 2.0 and the number of free carboxyl groups/mol was 0.25.

EXAMPLE 3

Preparation of compound 3.

A mixture of maleic acid anhydride (30 g), ethylene glycol (180 g), pentaerythritol (150 g) and 1,4-cyclohexane dicarboxylic acid (300 g) was heated at 210-220°C for 4 h under nitrogen gas. After cooling to 150°C, pyromellitic acid anhydride (30 g) was added, whereafter the reaction was allowed to continue at 160°C until the acid number 50 had been reached. An analysis of the thus obtained product showed that the number of free hydroxyl groups/mol was 2.88 and the number of free carboxyl groups/mol was 0.26.

EXAMPLE 4

Preparation of compound 4

A mixture of maleic acid anhydride (75 g), ethylene glycol (240 g), trimethylolpropane (105 g) and 1,4-cyclohexane dicarboxylic acid (300 g) was heated at 210-220°C under nitrogen gas. When the acid number had fallen to 50, the reaction mixture was cooled. An analysis showed that the number of free hydroxyl groups/ mol was 2.05 and the number of free carboxyl groups/mol was 0.21.

EXAMPLE 5

Antiredeposition effect

The antiredeposition effect of compounds Nos. 1, 2, 3 and 4 was examined by wash tests. Five mutually subsequent washes were carried out, whereafter the results were evaluated and compared with the effect of CMC. As a reference, use was made of sodium sulphate, which is inactive as an antiredeposition agent.

1. Tested detergent compositions:

	Reference (% by weight)	Compound 1-4 (% by weight)	CMC (% by weight)
Linear alkyl benzenesulphonate (the alkyl group contains approx. 11 carbon atoms)	8	8	8
Alkyl phenol with 9 carbon atoms and approx. 16 ethylene oxide groups	2.9	2.9	2.9
Soap	2.8	2.8	2.8
Sodium tripolyphosphate	35	35	35
EDTA	0.2	0.2	0.2
Sodium disilicate	10	10	10
Sodium perborate	20	20	20
Magnesium silicate	1.5	1.5	1.5
Compound 1-4	-	1	-
CMC	-	-	1
Sodium sulphate	to 100%	to 100%	to 100%

2. Equipment and material

2.1 Test washing machine of the agitator type ("Terg-o-tometer" from United States Testing Inc)

2.2 Photometric reflection measurer ("Elrepho" from Carl Zeiss)

2.3 Drying cabinet, lab. model

2.4 Detergent according to point 1 above with a dosage of 5 g/l (0.5 %)

2.5 Dirt load: 0.4 g particulate dirt (air filter dust)/l and 1.0 g synthetic skin grease/l is carried in the washing solution on cotton cloths on which the dirt is applied.

2.5.1 Preparation of dirt cloths: 0.2 g air filter dust and 0.5 g synthetic skin grease are applied on a 6 x 15 cm cotton cloth. The dirt is mixed and spread out on the cloth which is folded and joined together, heated for 5 min at 60°C and thereafter stored in a refrigerator at $\leq$+4°C.

2.6 Textile samples for measuring degree of greying. 3 sample pieces/l à 13 x 13 cm of each of:

Cotton 100% (405 Test Fabrics)
Polyester/cotton 65/35% (213 EMPA)
Polyester 100 % (Dacron 54 Test Fabrics)

3. Test execution

3.1 Reflective capacity - O-value - R_o

The test piece was folded in four and its reflective capacity was measured on both sides in order to obtain 3 measurement values. The mean value hereof was taken as O-value (R_o).

3.2 Washing procedure

1 litre of water was heated in the Terg-o-tometer with the lid on to 60°C under agitation (100 rpm). The hardness of the water was adjusted to 15°dH. The detergent was added and dissolved for 1 min, whereafter 3 samples of each of the textiles, as well as 1.4 g of dirt loading were placed in the machine. The washing program lasted for 35 min.

3.3 Rinsing and drying

The test pieces were rinsed, whereafter they were transferred to a clean bowl in which they were rinsed by hand for 3 min under running cold water (15-20°C, approx. 2.5°dH). Excess water was wrung out and the test pieces were dried on bars in a drying cabinet at 45-50°C for 25 min.

3.4 Reflective capacity - R_n. (n = number of washes)

The test pieces were folded in four and their reflective capacity was measured on both sides in order to obtain three measurement values. The mean value hereof was taken as the reflectance value (R_n).

3.5 Result calculation

$R_o - R_n = \Delta_n$ = greying after n number of washes.

3.6 Evaluation

The result is shown in the Table below.

It is apparent from the Table that the antiredeposition agent according to the invention has an extremely good greying-preventive effect on polyester fibres, whereas, on the other hand, CMC almost completely lacks such an effect. It is further apparent that the agent according to the invention also has a good effect on mixed textiles of polyester/cotton, while also in this case CMC almost totally lacks any greying-preventive effect. On pure cotton textiles, CMC displays the best greying-preventive effect, but it is worth noting that the agent according to the invention displays a marked greying-preventive effect also on such textiles.

Greying Δ_5

	Cotton 100 %	Polyester/cotton 65/35 %	Polyester 100 %
Reference	22.0	12.2	23.4
Reference + CMC	13.0	11.2	26.9
Compound 1	20.0	10.1	5.0
Compound 2	21.0	10.2	10.8
Compound 3	20.3	10.5	13.3
Compound 4	21.3	10.3	11.7

CLAIMS

1. Antiredeposition agent which consists of a low-molecular, multi-functional ester, characterized in that the ester is formed of multi-functional acids which are selected from among aliphatic, cycloaliphatic and aromatic divalent, trivalent and tetravalent carboxylic acids or mixtures thereof, and multi-functional alcohols which are selected from among aliphatic and cycloaliphatic divalent, trivalent and tetravalent alcohols or mixtures thereof, the ester containing from 1 to 6 acid units which are esterified with alcohol units, and the esterification being such that the ratio of the ester of free hydroxyl groups to free carboxyl groups is 2-30.

2. Antiredeposition agent according to claim 1, characterized in that it contains 1-3 acid units.

3. Antiredeposition agent according to claim 1 or 2, characterized in that the ratio between free hydroxyl groups and free carboxyl groups is 5-15.

4. Antiredeposition agent according to any one of claims 1-3, characterized in that the ester contains 1-3, preferably 2-3 free hydroxyl groups/mol.

5. Antiredeposition agent according to any one of claims 1-4, characterized in that the ester contains 0.1-0.5, preferably 0.2-0.4 free carboxyl groups/mol.

6. Antiredeposition agent according to claim 1, characterized in that the multi-functional acid is selected from among phthalic acid anhydride, isophthalic acid, adipic acid, maleic acid and trimellitic acid, or mixtures thereof.

7. Antiredeposition agent according to claim 1, characterized in that the multi-functional alcohol is selected from among ethylene glycol, 1,2 propanediol and diethylene glycol, or mixtures thereof.

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EUROPEAN SEARCH REPORT

Application number
EP 81 85 0004.3

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
X	DE -A1 - 2 846 984 (RHONE-POULENC IND.) * claims 1, 4, 5; page 10, paragraph 5; page 12, paragraph 5 * & GB - A - 2 007 692 --	1,6,7
P,X	GB - A - 1 563 808 (IMPERIAL CHEMICAL INDUSTRIES LTD.) * claims 1, 6, 15, 17, 19, 21 * --	1,6,7
	FR -A1 - 2 348 964 (IMPERIAL CHEMICAL INDUSTRIES LTD.) * claims 2 to 4 * & GB - A - 1 575 007 --	1,6,7
A	DE -A1 - 2 717 330 (DOW CHEMICAL CO.) & FR -A1 - 2 348 963 & US - A - 4 138 352 --	
A	GB - A - 1 505 798 (PROCTER & GAMBLE CO.) --	
A	DE - A - 2 301 728 (HENKEL & CIE GMBH) --	
A	DE - A1 - 2 834 073 (BASF AG) ----	

The present search report has been drawn up for all claims

CLASSIFICATION OF THE APPLICATION (Int. Cl.3)

C 11 D 1/72
C 07 C 69/07
C 07 C 67/08

TECHNICAL FIELDS SEARCHED (Int. Cl.3)

C 07 C 67/00
C 07 C 69/00
C 11 D 1/00
C 11 D 3/00

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons
&: member of the same patent family, corresponding document

Place of search	Date of completion of the search	Examiner
Berlin	31-03-1981	SCHULTZE