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(54) Titre : DETERGENT COMPOSITION.

(57) Abrégé :

Detergent products in semi-solid form, ie a gel, cream or paste, contain non-soap detergent active, a water-soluble salt, a detergent builder and water. The products are characterised by a composition which generates a pH in the range from 7.0 to 9.8 when mixed with deionised water at a weight ratio of 1:99. The use of such a composition enhances stain removal.

DETERGENT COMPOSITION

This invention relates to detergent compositions in semi-solid form, that is to say a gel, cream or paste. Such a detergent form is usually referred to as a "cream" and yet is usually sufficiently solid that it cannot be poured at ambient temperatures. It coheres together in a mass which can, however, be deformed by hand. Thus, this form is distinct from liquids, powders and shaped solid forms such as bars.

Such laundry detergent creams are marketed in some countries for fabric washing and are frequently used in a washing procedure during which the fabric is in contact with diluted detergent compositions for a relatively short time before it is rinsed.

Detergent active materials have often been considered to function most effectively under alkaline washing conditions. See for example Kirk-Othmer's Encyclopedia of Chemical Technology, vol 22. page 390. Consequently detergent compositions are formulated so that when brought into contact with water an alkaline wash liquor is generated. Laundry detergent creams have followed this general principle and commercial creams have contained alkaline salts so that when the cream is brought into contact with water, the liquid formed by dissolution is alkaline. Typically sodium carbonate and/or sodium silicate is included to raise the alkalinity to a pH in the range from above pH 10 eg. pH 11 or higher.

By contrast with the current practice of formulating for high pH we have now found that it is both possible and advantageous to formulate a detergent cream so that it gives a reduced alkaline pH when placed in water. We have found that compositions with satisfactory structure and

integrity during storage can be made, even though their content of salts, especially strongly alkaline carbonate and silicate, is sufficiently low that when brought into contact with water a pH of 9.8 or less develops.

We have also found that in use of such compositions with a relatively short duration of contact between the diluted composition and the fabric, formulation with lower pH leads to improved detergency against a range of stains, even including some stains for which reduction of pH has been found not to be beneficial when using a different product form and a longer duration of contact with the fabric.

Accordingly, the present invention provides a detergent composition in semi-solid form comprising:

(a) 10% to 45% by weight of non-soap detergent active;

(b) 3% to 30% by weight of water-soluble salts, at least some of which are detergency builders;

(c) 25% to 87% by weight of water characterised in that the composition generates a pH in the range from 7.0 to 9.8 when mixed with deionised water at a weight ratio of composition: water of 1:99 and allowed to dissolve as completely as possible at a temperature of 20°C.

The percentages of detergent active and water soluble salts refer to the anhydrous material and do not include any water taken up as water of hydration.

In practice the pH of a composition will not vary much with temperature, so that a pH value measured at any

temperature in the range from 15°C to 30°C will be adequately accurate.

It is preferred that the pH, measured at 20°C as stated above, lies in a range from 7.5 to 9.6. The pH may well lie above a lower limit of pH 8.0. Alternatively, or in addition, it may lie in a range not exceeding pH 9.3 or even pH 9.2.

In order to attain a lower pH than that which is conventionally obtained, the creams will desirably not contain much, if any, water soluble carbonate nor water soluble silicate, both of which are strongly alkaline.

In particular the composition may be formulated so as to contain not more than 3% by weight of water soluble carbonate, or indeed not more than 3% by weight of both water soluble carbonate and silicate.

Depending on the intended pH other less alkaline salts may be introduced to provide further control of the pH. Thus for instance sodium carbonate may be at least partially replaced with bicarbonate or borax.

In use, of course, the proportions of mixing with water are not controlled and deionised water is not used. Nevertheless the pH which is generated in use will be adequately related to that measured under the stated conditions, since it is largely controlled by the salts in the composition.

The water soluble salts in the composition may include phosphate builder salts which can help to buffer the pH which is developed on mixing with water.

Another optional, although desirable, feature is to incorporate bleach, in particular sodium sulphite, to enhance the laundering performance. We have found that this can be used successfully in the pH range specified by this invention.

Materials useful in compositions of this invention will now be discussed in turn:

Detergent active

As already mentioned, the composition includes non-soap detergent active in an amount from 10 to 45wt% of the overall composition. It is envisaged that the amount will generally range from 12 to 40wt% and a particularly envisaged range is from 15 to 50 wt%.

Detergent actives useable in the present invention may be found in the general classes of anionic, nonionic, amphoteric and zwitterionic actives. Generally, non-soap anionic detergent active will be the main detergent active present. If any other categories of detergent active are present, these will typically be in minor amounts relative to the anionic detergent active.

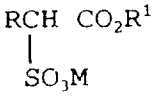
Anionic detergent actives which are particularly envisaged for use in the present invention are alkyl benzene sulphonates of formula

$$R{-\!-}C_6H_4{-\!-}SO_3M$$

primary alcohol sulphates of formula

$$ROSO_3M$$

and/or fatty acyl ester sulphonates of formula



in each of which R is a primary alkyl group containing 18 to 22 carbon atoms preferably 10 to 18 carbon atoms, R^1 if present is a primary alkyl group containing 1 to 6 carbon atoms preferably 1 to 4 carbon atoms, and M is a cation such that the detergent active material is water soluble.

Other detergent actives which may be used include alkane sulphonates and ethoxylated alcohol sulphates. If nonionic detergent active is used it will generally be ethoxylated alcohol. Fatty acyl alkanolamides may also be employed.

It is possible within the scope of the invention to include soap but it would generally be absent because it inhibits the formation of lather by the non-soap detergent active. Consequently it is preferred that if soap is present at all, the amount of it does not exceed 2% by weight of the composition.

Water soluble salts

These may have a function in the composition, especially as a detergency builder or as a bleach. However, inert salts such as sodium sulphate may also be present. The amount of water soluble salts is preferably at least 5% by weight of the composition and may well not exceed 20% by weight.

Detergency builder

At least some of the water soluble salts are required to be detergency builder salts. Preferred is 3% to 30% by weight, better 3% to 20% by weight of an alkali metal orthophosphate, pyrophosphate or tripolyphosphate. Other water soluble builder salts are organic builders, eg.

sodium nitrilotriacetate, sodium tartrate, sodium citrate and sodium carboxymethylsuccinate.

In addition to the use of water soluble builder, water-insoluble aluminosilicate ion exchanger, for example zeolite 4A, may also be included.

Water insolubles

It is desirable to incorporate a soluble aluminium salt, such as aluminium sulphate into the composition together with sufficient sodium silicate that insoluble aluminosilicate forms in situ in the composition. This is valuable in enhancing the structure and stability of the composition. British patent specification 2099013 describes the analogous incorporation of such aluminosilicate into rigid bars.

Also, a water insoluble filler other than aluminosilicate may be included in the composition: this may be a clay such as kaolin or bentonite.

We have now found that it is possible to obtain a satisfactory stability during storage, without undue hardness of the composition, by incorporating aluminosilicate by formation in situ and also incorporating other water-insoluble filler in a weight ratio lying in a range from 70:30 to 30:70.

The water-insoluble material other than aluminosilicate is preferably clay so that the proportions of aluminosilicate to clay lie in the range 7:3 to 3:7. A preferred range is 6:4 to 4:6.

The aluminosilicate, as mentioned above, is desirably formed in situ in the composition by incorporating a soluble aluminium salt such as aluminium sulphate in the

composition and also sodium silicate. When aluminium sulphate is used as the aluminium salt the amount of aluminosilicate which forms is approximately equal to the weight of an aluminium sulphate from which it is formed, provided that there is sufficient sodium silicate to give complete conversion of the soluble aluminium salt into the insoluble aluminosilicate.

Hydrotrope

It is known to incorporate hydrotrope into detergent creams. Such hydrotropes include short chain alkyl benzene sulphonates such as sodium toluene sulphonate. Preferred, however, is urea.

A considerable advantage of this invention is that reduction of the pH of the composition leads to a surprising improvement in the stability of urea in a detergent cream.

Bleach

The water-soluble alkali metal salts of those sulphur oxo acids which are reducing agents may be included in the composition as bleaches. Preferred is to incorporate from 1 to 15% by weight of such material, better at least 2% or even at least 5% by weight.

Other ingredients

The composition of the invention may also contain other detergent additives in conventional amounts. Such additives include antiredeposition agents such as sodium carboxymethyl cellulose, colouring materials, fluorescers, photobleaches, germicides, opacifiers, humectants such as glycerol, perfumes and alternative bleaches. Enzymes may also be included, notably proteases, lipases and amylases.

Production

A semi-solid detergent composition can be produced by adding the constituents to the water which will be present in the eventual composition, and mixing.

A suitable procedure is to heat all the water, and dissolve it in the water-soluble builder, other solid electrolyte (if used) and sodium carboxymethyl cellulose (if used) while mixing under conditions of high shear. When these components have dissolved, alkaline silicate (if any) is added, followed by detergent active and alkanolamine (if any). Finally the sulphite (or bisulphite or metabisulphite), any fluorescer and perfume are added.

The detergent actives should be fully neutralised before the sulphite bleach is added, to avoid decomposition of the bleach during manufacture. The sulphite is therefore added at the end of the procedure.

In the examples which follow all percentages are by weight unless stated otherwise.

EXAMPLES

A number of creams were made in accordance with formulations as set out in the following TABLE 1. The pH generated by each formulation was assessed by dispersing it in deionised water at a concentration of 1.0% by weight ie a composition: water ratio of 1:99 by weight. The dispersion was allowed to stand for long enough to allow all soluble materials to dissolve after which the pH of the dispersion was measured at ambient room temperature of 20°C (small variations in temperature will not effect the pH to any noticeable extent).

TABLE 1

TEST CREAM COMPOSITIONS					
Product	**1**	**2**	**3**	**4**	**5**
Ingredient	**% by weight**				
Sodium alkyl benzene sulphonate	22	22	35	35	22
Sodium carbonate	-	5	-	5	-
Sodium alkaline silicate (anhydrous basis)	3	3	2	2	3
Aluminium sulphate (anhydrous basis)	4	4	3	3	4
Kaolin	6	1	-	-	1
Urea	1	1	1	1	1
Sodium pyrophosphate	6	6	6	6	6
Sodium sulphite	-	-	-	-	5
Water, minors etc.	to 100				
pH (1% dispersion)	9.1	10.4	9.3	10.1	9.2

A number of cotton sheet test cloths (250 by 375 cms) were stained with a variety of different stains on different area of the test cloth. The stains were red wine, banana, blackberry, grass, tea, coffee, coffee/milk, tea/milk and tea/milk/sugar.

The various creams were then used to wash the test cloths using a standardised procedure commonly used with detergent creams.

The test cloth was immersed in a quantity of deionised water at a liquor to cloth ratio of 7:1. The wetted test cloth was squeezed out, reimmersed and squeezed out a second time and then treated with the test cream. The cream was spread by hand on the cloth until the amount of detergent composition transferred to the cloth was equivalent to 4% by weight of the dried cloth. The

treated test cloth was rubbed 40 times over a period of 30 seconds. After this time it was squeezed and rinsed once in clean, cold water.

The reflectance of each stained area of the test cloth was measured at 460nm before and after washing.

EXAMPLE 1

Assessments of stain removal

In this example, the stain removal of a cream according to the invention (Product 1) was compared with a conventional cream formulation containing sodium carbonate (Product 2). The results in Table 2 demonstrate that the product according to the invention has improved stain removal compared to the conventional product.

TABLE 2

Stain type	**Reflectance Change (R460)**	
	Product 1	**Product 2**
Red Wine	10.6	8.8
Banana	9.6	5.9
Blackberry	19.3	13.6
Grass	20.3	16.0
Tea	7.0	2.9
Coffee	13.6	8.1
Coffee/Milk	20.7	18.4
Tea/Milk	13.2	5.7
Tea/Milk/Sugar	13.9	8.6

EXAMPLE 2

Assessments of stain removal

This example also demonstrates the improvement in stain removal of a composition according to the invention (Product 3) compared to a conventional composition (Product 4). These products have a high percentage of branched chain alkyl benzene sulphonate.

TABLE 3

Stain type	Reflectance Change (R460)	
	Product 3	Product 4
Red Wine	8.6	7.3
Banana	18.5	15.1
Blackberry	5.9	3.3
Grass	22.1	16.1
Tea	5.4	3.4
Coffee	10.0	9.2
Coffee/Milk	22.9	21.9
Tea/Milk	10.8	8.9
Tea/Milk/Sugar	13.9	12.6

EXAMPLE 3

Assessments of stain removal

In this example the effect on stain removal of combining low pH and the bleach sodium sulphite was examined.

Stain Type	Reflectance Change (R460)		
	Product 5	Product 1	Product 2
Mango	34.0	27.8	26.9
Coffee/Milk	35.0	32.1	32.1
Banana	23.9	14.9	13.9
Tea/Milk	9.5	10.1	6.2
Rust	27.9	24.9	23.1
	pH = 9.0	pH = 9.0	pH = 10.2

It can be seen that for four stains the presence of the bleach gave an added improvement.

EXAMPLE 4

Assessments of stability

Samples of products 1 and 2 were stored at 30°C. After one week the product 2 had a noticeable smell of ammonia whereas product 1 did not, indicating that the lower pH of product 1 was remarkably improving the stability of urea.

EXAMPLE 5

Two series of compositions were prepared. In each composition the basic formulation was:

Ingredient	% by weight
Sodium alkyl benzene sulphonate	22
Sodium alkaline silicate)	
Aluminium sulphate)	see below
Kaolin)	
Urea	1
Sodium pyrophosphate	6
Water, minors etc	balance to 100%

In these compositions the proportions of kaolin and aluminosilicates were varied. The quantity of sodium

alkaline silicate was varied also to correspond with the quantity of aluminium sulphate. The compositions were balanced to 100% by adjusting the weight of water. In one series of compositions the total of kaolin and aluminosilicate was 7.5% by weight of the composition, in the second set it was 12% by weight of the composition.

The compositions were cycled repeatedly between 20°C and 30°C. After 20 cycles the compositions were assessed for the extent of separation on a scale from 0 to 5 as follows:

0 = no change in appearance or mobility
1 = slight change in appearance or mobility
2 = some change but no liquid droplets visible
3 = some liquid visible
4 = layer of liquid on top of product
5 = deeper layer of liquid on product

Values up to 2 are satisfactory. The results were:

Total Kaolin and aluminosilicate:	7.5%	12%
Kaolin: Al-Si ratio		
100 : 0	5	3
80 : 20	3	2
60: 40	2	1-2
40: 60	1-2	0
20 : 80	1-2	0
0 : 100	1	0

Compositions without kaolin were sufficiently hard that it was very difficult to scoop a portion out of a container using only the fingers (which is the general practice for removal). Compositions without aluminosilicate were soft

and difficult to apply to fabric, especially the composition with 7.5% kaolin and no aluminosilicate.

Compositions with a combination of both materials, especially in the range 70:30 to 30:70 better 60:40 to 40:60 gave a good combination of handling properties and resistance to separation.

CLAIMS

1. A detergent composition in semi-solid form comprising:

(a) 10% to 45% by weight of non-soap detergent active;
(b) 3% to 30% by weight of water-soluble salts, at least some of which are detergency builders; and
(c) 25% to 87% by weight of water,

characterised in that the composition generates a pH in the range from 7.0 to 9.8 when mixed with deionised water at a weight ratio of composition: water of 1:99 and allowed to dissolve as completely as possible at a temperature of 20°C.

2. A detergent composition according to claim 1 wherein the water soluble salts comprise from 3% to 30% by weight (based on the whole composition) of a detergency builder which is an alkali metal orthophosphate, pyrophosphate or tripolyphosphate, optionally together with other water soluble salts.

3. A detergent composition according to claim 1 further comprising from 1 to 15% by weight of water-insoluble material.

4. A detergent composition according to claim 1 comprising from 5 to 15% in total water-insoluble material consisting of aluminosilicate and other material in weight ratio lying in a range from 7:3 to 3:7.

5. A detergent composition according to claim 4 wherein the ratio or aluminosilicate to other material is in the range 6:4 to 4:6.

6. A detergent composition according to claim 1 further comprising from 0.5 to 5% by weight of hydrotrope.

7. A detergent composition according to claim 6 wherein the hydrotrope is urea.

8. A detergent composition according to claim 1 which does not contain more than 3% by weight of water soluble carbonate.

9. A detergent composition according to claim 1 wherein the pH lies in a range from 7.5 to 9.6.

10. A detergent composition according to claim 9 wherein the pH lies in a range from 8.0 to 9.3.

11. A detergent composition according to claim 1 including from 2 to 15% by weight of alkali metal sulphite, bisulphite or meta-bisulphite.

12. A method of washing fabrics comprising contacting the fabric with a composition according to any one of the preceding claims, or a liquor formed by dilution of the composition, followed by rinsing the fabric after a period of not more than 5 minutes.