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(54) **Detergent composition.**

(57) A detergent composition has a high (≧ 30%) content of anionic detergent yet has acceptable physical properties for use as part or all of a retail product. The anionic detergent is mixed with a particulate filler which has high oil absorbency. The filler is intimately distributed within the particles of the composition.

DETERGENT COMPOSITION

FIELD AND BACKGROUND OF THE INVENTION

This invention relates to the particulate detergent compositions containing relatively high levels of detergent active and furthermore where the detergent comprises a high level of anionic detergent, at least 30% by weight of the composition. Such compositions may in particular be suitable for cleaning fabrics, although they may be intended for other uses. This invention also relates to the production of such compositions.

Detergent compositions containing lower levels of anionic detergent active are commonplace, and are often prepared by spray drying as is well known. At first sight it might be supposed that there would be no difficulty in making compositions with higher concentrations of anionic detergent because many anionic detergent active materials can be prepared in more or less solid form consisting of substantially pure anionic detergent, or at least containing a very high percentage of anionic detergent.

However, such materials tend to be sticky and to cake together whereas products which are suitable for retail sale are required not to be sticky and to be free flowing. A sticky solid with a tendency to cake is of course inconvenient during manufacture as well as at the time of use.

In fact it is difficult to produce a particulate solid which both contains a high proportion of detergent active and also has satisfactory properties for use as part or the whole of a product suitable for retail sale.

SUMMARY OF THE PRIOR ART

US 4515707 (Brooks) discloses a procedure in which anionic detergent acid is neutralized and mixed with a powdered ingredient to produce a powder which is described as dry. This is used subsequently as a raw material for the production of detergent bars. The powdered ingredients which are referred to can be made with varying absorbencies and the document does not disclose materials of unusual absorbency.

US 4213874 (Williams et al) discloses the production of aluminosilicates which have an oil absorbtion of at least 75ml/100gram. It is disclosed that they may be used to absorb nonionic detergents in detergent products. US 4707290, GB 1485371 and GB 1591518 disclose the use of absorbent solids to act as carriers for nonionic detergents. Nonionic detergents are a different problem to anionic detergents in that the nonionic materials are generally liquids (which need to be made into solid form) whereby anionic detergents are generally solids in their own right.

It is known to apply powdered materials to the surface of a particulate solid to reduce stickiness and enhance its abilities to flow as a powder. This however is merely a surface treatment.

THE INVENTION

We have now found that the flow properties and caking resistance of detergent powders containing a high level of anionic detergent can be improved by incorporating a particulate filler with a relatively high oil absorption value.

Accordingly, in a first aspect, this invention provides a particulate detergent composition, the particles of which contain at least 30% by weight of anionic detergent active and also contain a particulate filler with an oil absorption value of at least 100ml/100g, this filler being distributed within the particles of the composition in intimate mixture with the detergent active, the amount of the particulate filler being such that the weight ratio of the filler to anionic detergent active lies in the range from 1:10 to 1:1, more preferably 1:8 to 2:3.

This ratio range signifies that the amount of filler is not greater than the amount of anionic detergent active.

It is preferred that the filler has a mean particle size not greater than 20 micrometres.

In a second aspect the invention provides a process of preparing a detergent composition which process comprises incorporating a particulate filler into a fluid or semi-solid composition containing anionic detergent active so that the filler is intimately mixed with the anionic detergent, which particulate filler has an oil absorbtion value in excess of 100ml/100gram, and forming the resultant mixture into a particulate composition with the filler distributed within the particles of the composition, the amounts of anionic detergent active and filler being such that the composition contains at least 30 wt% of anionic detergent and has a weight ratio of filler to detergent active ranging from 1:10 to 1:1.

DETAILED DESCRIPTION

Test for oil absorbency

As stated above, the present invention contains particulate filler with an oil absorption value which is equal to, or exceeds, a minimum value.

The oil absorption value of the filler is to be determined by the following test which is in accordance with British Standard 3483 : Part B7 : 1982. The test for oil absorption is performed by placing a weighed sample of the test powder on a plate and then adding linseed oil from a burette. The oil is added a few drops at a time. After each addition the powder is mixed vigorously with the oil using a palette knife. Addition of oil is continued until a paste of smooth consistency is formed. The paste should just spread without cracking or crumbling. The oil absorption value is expressed as the volume (ml) of oil absorbed per 100 gram of powder.

Applicability of compositions

A detergent composition according to the invention may be marketed directly as a washing product. Alternatively it can be mixed with other particulate material to form a finished product. In particular, a particulate detergent composition according to the invention may be mixed with a second particulate composition which contains other constituents of a final detergent composition, such as detergency builders. There are various possibilities for such a second composition. It might contain no detergent active or very little. It might contain a substantial quantity of detergent active but nevertheless a lower proportion than in a composition according to this invention which is mixed with it. Admixing the composition in accordance with the invention would then serve to increase the overall proportion of detergent active. There could even be a commercial advantage in circumstances where admixing a composition in accordance with this invention did not increase the overall proportion of detergent active - for instance by achieving beneficial physical properties or by enhancing overall production from available process plant.

Production routes

Production of compositions in accordance with this invention may be accomplished by conventional routes for the manufacture of particulate detergent compositions with a high level of detergent active, provided there is a stage when the detergent active is in a fluid or semi-solid form. The particulate filler is mixed with the detergent active at this stage and leads to an improvement in the properties of the particulate composition which is produced. In some instances a particulate state would not be achieved without the filler.

If the overall process entails neutralization, the filler can be mixed with the acid form of the detergent active before neutralization. The filler may even be used as a base to neutralise the acid form of the detergent active, i.e. part of the material used as filler may serve to effect neutralisation. Another possibility is to neutralise the active and mix the filler with the resulting neutralised paste before this becomes solid.

A fluid or semi-solid mixture containing the detergent active and the filler may be dried to solidify it, for example by means of a drum dryer. A viscous dough may be produced with a formulation such that the dough can be extruded but will then solidify into a hard solid which can be comminuted to desired particle size.

One preferred method of producing compositions of this invention is by neutralizing an acid form of an anionic detergent active with an alkali metal oxide, hydroxide or carbonate (which may be a true carbonate, bicarbonate or sesquicarbonate) to produce a viscous dough, mixing the particulate filler with this dough, allowing the dough to harden to a solid and comminuting the solid. Neutralization may be effected in the presence of little or no added water. Alternatively there may be some deliberate addition of water: this can lead to a solid which is already in equilibrium with atmospheric humidity. Generally, the amount of water added (if any) is not more than 10%, more preferably not more than 5%, by weight based on the total weight of acid detergent and carbonate.

Such neutralization and admixing of filler can be carried out in various types of high shear mixer. One possibility is a Z-blade mixer, another possibility is a cavity transfer mixer whose use as a chemical reactor is disclosed in our European patent application 194812, yet another possibility is a twin screw extruder. Other intensive mixers which may be used consist of vessels which contain rotating blades for mixing and high speed knives for dispersing, manufactured for example by Lödige (Trade Mark) ex Morton Machine Co Ltd, Scotland.

If production is by a route which entails neutralization of the acid form of an anionic detergent active, other detergent active may also be mixed in. For example some preneutralised detergent active or nonionic detergent active may be mixed in.

When the powder has been made it may be given a surface coating of a flow-improving aid which may itself be a particulate solid having the oil absorption property required for the filler used in this invention. Use of such materials as a surface coating is conventional. The examples below demonstrate that it does not, by itself, achieve the results achieved by the invention.

Materials : Detergent Active

As mentioned above compositions according to this invention must contain at least 30% by weight of active detergent. Preferably they contain more, e.g. at least 40% or even at least 55%. The amount of detergent active present may range as high as 90% by weight of the composition.

Various detergent actives may be utilized, selected from the conventional categories of anionic, nonionic, cationic and amphoteric. Preferably anionic detergent active predominates; even if detergent active from another category is present the anionic detergent active may itself provide 30%, 40% or even 55% or more of the composition.

Specific examples of anionic detergent actives useful in this invention are: linear and branched alkyl benzene sulphonates, alkane sulphonates, secondary alcohol sulphates, primary alcohol sulphates, alpha olefin sulphonates, alkyl ether sulphates, fatty acyl ester sulphonates, and mixtures of these. The invention is particularly applicable when at least part of the detergent active is alkyl benzene sulphonate, or a mixture thereof with fatty acyl ester sulphonate or primary alcohol sulphate.

Materials : Particulate Filler

As stated above the filler should have an oil absorbency, measured according to the test stated, of at least 100ml/100g. Preferably it is higher such as at least 150ml/100g, better at least 200ml/100g and most preferably at least 300ml/100g.

The filler may be water soluble but is more likely to be water insoluble.

Preferably the mean particle size of the filler is not over 20 micrometres, better not over 10 micrometres. A small particle size is especially desirable for an insoluble filler, since it facilitates rinsing the filler away after a detergent composition has been used. Small particle size increases the speed of dissolution of a soluble filler. An alternative way to state desirable particle size is that the particle size distribution includes substantially no particles larger than 50 micrometres. These particles however will generally be aggregates of smaller particles, typically having a size in the range from 5 to 200 nanometres and predominantly (or even wholly) in the narrower range 10 nanometres to 100 nanometres. Such smaller particles can be distinguished by electron microscopy.

A variety of materials are available with suitable particle size and oil absorbency. Suitable inorganic materials tend to be finely divided solids obtained by precipitation. Materials can be produced in such form include silica, aluminosilicates, calcium silicates, magnesium silicates and calcium carbonate. Other materials which can be suitable, subject to testing their oil absorbency, are diatomaceous earths and finely divided cellulosic fillers.

The amount of filler included in the composition will generally range from 3% to 50% by weight, usually 5% to 40%.

Other materials may be included in addition to the detergent active and specified filler, for example detergency builder, alkaline salts or other filler of lesser oil absorbency. A small quantity of moisture will almost always be present.

EXAMPLES

Examples I-V and Comparative Examples A-C

A number of compositions and comparative compositions were prepared using a standard procedure as follows.

Linear alkyl benzene sulphonic acid with an average C_{13} alkyl chain length was charged to a Z-blade mixer. Temperature was maintained at 80 °C. Sodium carbonate was added over ten minutes with continuous mixing during which time carbon dioxide was evolved. A particulate filler was then added over a period of 15 minutes and mixing continued for 5 minutes.

The dough produced by this procedure was removed from the mixer and cut into pellets. These were allowed to cool to ambient temperature, hardening as they did so. The pellets were milled into a powder. This was mixed with 2% by weight of a conventional flow aid which coated the surfaces of the powder particles.

The mean particle size, bulk density and dynamic flow rate of the resulting powders were tested. Their content of sodium alkyl benzene sulphonate was checked analytically and found to be approximately 60% by weight, except in Example 5 where the content was approximately 52% by weight. The dynamic flow rate, in ml/s, was measured using a cylindrical glass tube having an internal diameter of 35mm and a length of 600mm. The tube was securely clamped with its longitudinal axis vertical. Its lower end was terminated by means of a smooth cone of polyvinyl chloride having an internal angle of 15° and a lower outlet orifice of diameter 22.5mm. A beam sensor was positioned 150mm above the outlet, and a second beam sensor was positioned 250mm above the first sensor.

To determine the dynamic flow rate of a powder sample, the outlet orifice was temporarily closed, for example, by covering with a piece of card, and powder was poured into the top of the cylinder until the powder level was about 100mm above the upper sensor. The outlet was then opened and the time t -(seconds) taken for the powder level to fall from the upper sensor to the lower sensor was measured electronically. The result is the tube volume between the sensors, divided by the time measured.

Caking resistance of the particles and their hardness after exposure to air was tested by the following procedure: The powder was spread in a thin layer in a dish and exposed to atmosphere at 37°C and 70% relative humidity. After exposure for one week the powder was graded for feel. Also a sample of the powder which had been exposed was compressed under a standard load in a 2cm diameter cylindrical die to form a pellet. The hardness of the material in this pellet was tested with a cone penetrometer. The cone had an angle of 9° 10′ and was applied under 100 gram load for 10 seconds.

The compositions of these examples and comparative examples are set out in Tables 1 and 2 below. In the case of comparative example A an increased quantity of sodium carbonate was used rather than a separate particulate filler. In other words a part of the sodium carbonate, having an oil absorption value of 63ml/100g, constituted the particulate filler. In this comparative example the sodium carbonate was added over a period of 15 minutes in view of the greater quantity used.

The various solids were nominally dry, which in practice means that they contained a small percentage of absorbed moisture.

TABLE 1

Components Charged in the Z-blade Mixer (Kg)								
	I	II	III	IV	V	A	B	C
Alkyl benzene sulphonic acid (1)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Sodium carbonate (2)	0.2	0.2	0.2	0.4	1.0	0.8	0.2	0.2
Water	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Socal U3 (3)	0.6	-	-	-	-	-	-	-
Alusil ET (4)	-	0.6	-	-	-	-	-	-
Microsil GP (5)	-	-	0.6	0.4	0.12	-	-	-
Kaolin (6)	-	-	-	-	-	-	0.6	-
Durcal 40 (7)	-	-	-	-	-	-	-	0.6

(1) Sulphonated Dobane 113, ex Shell (1) Sulphonated Dobane 113, ex Shell
(2) Light Soda Ash, ex ICI (2) Light Soda Ash, ex ICI
(3) Calcium Carbonated, ex Solvay (3) Calcium Carbonate, ex Solvay
(4) Aluminosilicate, ex J Crosfield and Sons (4) Aluminosilicate, ex J Crosfield and Sons
(5) Silica, ex J Crossfield and Sons (5) Silica, ex J Crosfield and Sons
(6) Speswhite grade, ex English China Clays (6) Speswhite grade, ex English China Clays
(7) Calcium Carbonate, ex Sturge. (7) Calcium Carbonate, ex Sturge.

TABLE 2

Properties of Materials Produced								
	I	II	III	IV	V	A	B	C
Mean particle size (µm)	515	505	465	485	510	500	515	525
Bulk density (Kg/m^3)	668	652	654	664	700	676	668	650
Dynamic flow rate (ml/sec)	75	80	96	96	90	75	75	70
Penetration of compact pellet after exposure (mm)	14	6.8	2.4	3.5	4.2	19	20	22
Feel of the powder after exposure*	S	MS	MC	MC	MC	VS	VS	VS
Oil absorption value of the filler (ml/100g)	120	200	330	330	330	63**	51	25

* S = Soft, MS = Moderately Soft, MC = Moderately Crisp, VS = Very Soft

** Oil absorption value of the light soda ash.

It can be seen that below an oil absorption value of 100ml/100g the properties of the powder are not much affected by the oil absorption value of the filler whereas considerable improvements are observed at higher oil absorption values.

In each case the conventional flow aid used to provide a surface coating on the particles was Alusil ET. The inferior results with the comparative examples demonstrate that a conventional dusting or surface coating with a flow aid does not itself achieve the benefit of this invention.

Examples 6 and 7, Comparative Examples D and E

These Examples commence using pastes, i.e. previously neutralised detergent active. The procedure was as follows.

Sodium primary alcohol sulphate paste or sodium alkyl benzene sulphonate paste was charged to a Z-blade mixer. Temperature was maintained at 80° C. Sodium carbonate was added over five minutes with continuous mixing. A particulate filler was then added over a period of 15 minutes and mixing continued for 5 minutes.

The dough produced by this procedure was removed from the mixer and cut into pellets. These were dried and allowed to cool to ambient temperature, hardening as they did so. Excepting pellets from Example E, which could not be milled as they were too soft, the pellets were milled into a powder. This was mixed with 2% by weight of a conventional flow aid (Alusil ET).

The physical properties were determined as for Examples 1-5. The active contents were measured analytically and are shown in Table 4.

TABLE 3

Components charged in the Z-blade mixer				
	VI	D	VII	E
Sodium primary alcohol sulphate paste (1)	1.0	1.0	-	-
Sodium alkyl benzene sulphonate paste (2)	-	-	1.0	1.0
Sodium carbonate (3)	0.25	0.4	0.45	0.6
Microsil GP (4)	0.15	-	0.15	-

(1) Derived from coconut oil, active content 62%.

(2) Derived from Dobane 113, ex Shell, active content 75%.

(3) Light Soda Ash, ex ICI.

(4) Silica, ex J Crosfield and Sons.

TABLE 4

Properties of Materials Produced				
	VI	D	VII	E
Moisture content after drying (%)	15.3	14.1	3.1	2.1
% Active	52	52	54	54
Mean particle size (um)	400	355	630	- (1)
Bulk Density (Kg/m^3)	560	585	680	-
Dynamic flow rate (ml/sec)	80	75	90	-
Penetration of compacted pellet after exposure (mm)	0.8	2.3	5.5	-
Feel of the powder after exposure (3)	C	MS(2)	MC	-
Oil absorption value of the filler (ml/100g)	330	63	330	63

(1) Could not be satisfactorily comminuted.
(2) Formed some lumps.
(3) C = Crisp, MC = Moderately Crisp, MS = Moderately Soft.

Once again it was apparent that incorporation of filler with high oil absorption value led to powders with enhanced physical properties. Examples 7 and E are an instance where a particulate solid was not achieved without the filler.

Claims

1. A particulate detergent composition, the particles of which contain at least 30% by weight of anionic detergent active and also contain a particulate filler with an oil absorption value of at least 100ml/100g, this filler being distributed within the particles of the composition in intimate mixture with said detergent active, and the weight ratio of the filler to the anionic detergent active lying in the range from 1:10 to 1:1.
2. A composition according to claim 1 wherein the filler has an oil absorption value of at least 200ml/100g.
3. A composition according to claim 1 or claim 2 wherein the filler has a mean particle size not greater than 20 micrometres.
4. A composition according to claim 3 wherein the filler is water-insoluble.
5. A composition according to any one of the preceding claims wherein the filler has a particle size distribution such that substantially no filler particles have a size greater than 50 micrometres.
6. A mixture comprising a composition according to any one of the preceding claims together with other solid particulate material.
7. A mixture according to claim 6 comprising said filler in an amount from 3% to 50% by weight of the composition.
8. A process of preparing a detergent composition which process comprises incorporating a particulate filler into a fluid or semi-solid composition containing anionic detergent active, so that the filler is intimately mixed with the anionic detergent active, said particulate filler having an oil absorbtion value in excess of 100ml/100grams, and forming the resultant mixture into a particulate composition with the filler distributed within the particles of the composition, the amounts of anionic detergent active and filler being such that the composition contains at least 30 wt% of anionic detergent active and has a weight ratio of filler to anionic detergent active ranging from 1:10 to 1:1.
9. A process according to claim 8 comprising neutralizing the acid form of anionic detergent active with an alkali metal carbonate salt to form a semi-solid composition containing the neutralized detergent active, said filler then being added to the said composition, the process thereafter comprising allowing the resulting mixture to harden, and comminuting it.
10. A process according to claim 9 wherein the amount of water (if any) added to the acid form of the anionic detergent active and the alkali metal carbonate salt is not more than 10% by weight based on the total of the acid and the carbonate salt.